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**A**

**DICTIONARY OF CHEMISTRY.**

**VOL. II.**

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A DICTIONARY  
OF  
C H E M I S T R Y

AND THE  
ALLIED BRANCHES OF OTHER SCIENCES.

*Founded on that of the late Dr. Ure.*

BY  
HENRY WATTS, B.A., F.C.S.

EDITOR OF  
'THE JOURNAL OF THE CHEMICAL SOCIETY.'

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IN FOUR VOLUMES.

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CONHYDRINE—GYTGE.

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## DICTIONARY OF CHEMISTRY.

**CONHYDRINE.**  $C^8H^{11}NO$ , or  $C^8H^9NO^2$ . (Wertheim, *Wien. Akad. Ber.* xxii. 113.)—This alkaloïd, which has the composition of a hydrate of conine ( $C^8H^{11}N.H^2O$ ), exists, together with conine, in the flowers and ripe seeds of hemlock (*Conium maculatum*). It is extracted by a process which will be described under CONINE, and purified from adhering conine by pressing the product after it has been submitted to a low temperature (by means of a freezing mixture), and subsequently by repeated recrystallisation from ether. 100 kilogr. of fresh flowers yield 6 grammes of pure crystals.

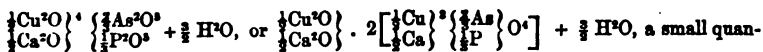
Conhydrine crystallises in laminæ having a pearly lustre and splendid iridescence; they melt at a gentle heat and sublime below  $100^{\circ}C$ . It has a slight odour, which increases when the substance is volatilised, and closely resembles that of conine. Its aqueous and alcoholic solutions have a strong alkaline reaction. Its physiological action is narcotic, but less powerful than that of conine.

1 pt. of conhydrine, heated to  $200^{\circ}C$ . for an hour and a half with 3 pts. of anhydrous phosphoric acid in a glass tube, decomposes into conine and water.

Conhydrine neutralises acids, expels ammonia from its compounds, but appears to be separated from its salts by conine. The hydrochlorate is uncrystallisable.

**Chloroplatinate,**  $C^8H^{11}NO.HClPtCl^2$ .—An alcoholic solution of conhydrine neutralised with hydrochloric acid is mixed with alcoholic dichloride of platinum, care being taken to avoid an excess of the latter, and the whole is placed over sulphuric acid in vacuo; when crystals begin to form, the solution is removed to the air and allowed to evaporate, and the crystals are washed, first with ether-alcohol, then with ether. The salt crystallises in hyacinth-red tablets, from 1 to 4 millim. in length, belonging to the trimetric system. It gave by analysis 27.58 per cent. C, 5.31 H, 4.56 N, and 28.04 Pt, the formula requiring 29.47 C, 5.15 H, 4.01 N, and 28.33 Pt.

**CONICHALCITE.** An arseno-phosphate of copper and calcium, containing also a small quantity of vanadic acid, found at Hinajosa de Cordova in Andalusia. It forms reniform masses of pistachio-green colour inclining to emerald green, and yielding a streak of the same colour. Hardness = 4.5. Specific gravity = 4.123. Subtranslucent. Brittle. Fracture splintery. It contains, according to Fritzsche (Pogg. Ann. lxxvii. 139), 30.68 per cent.  $As^2O^3$ , 8.81  $P^2O^5$ , 1.78  $V^2O^5$ , 31.76  $Cu^2O$ , 21.96  $Ca^2O$ , and 5.61 water, whence it may be regarded as



tity of the arsenic or phosphoric acid being replaced by vanadic acid. (Dana, ii. 421; Rammelsberg, p. 376.)

**CONINE.** *Coniine, Cicutine*,  $C^8H^{11}N$ , or  $C^8H^9N$ .—A volatile alkaloïd which forms the poisonous principle of hemlock (*Conium maculatum*). It was discovered in 1827 by Giesecke (Brandes' Arch. Pharm. xx. 97), but was first prepared in the pure state by Geiger in 1831 (Mag. Pharm. xxxv. 72, 259; xxxvi. 159). Ortigosa (Ann. Ch. Pharm. xlii. 313) assigned to it the formula  $C^8H^{11}N$ ; Blyth (Chem. Soc. Qu. J. i. 345) regarded it as  $C^7H^{11}N$ . The formula  $C^8H^{11}N$ , according to which conine is isomeric with cyanide of œnanthyl or capronitrile,  $C^7H^{11}.CN$ , was proposed by Gerhardt and adopted by v. Planta and Kékulé (Ann. Ch. Pharm. lxxxix. 129),

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who have shown that conine exhibits the characters of a secondary monamine  $(\text{C}^{\text{H}}\text{H}^{14})\text{N}$ , or perhaps  $(\text{O}^{\text{H}}\text{H}^2)\text{N}$ .

The last formula, which represents conine as containing the radicle butyrosyl  $\text{C}^{\text{H}}\text{H}^7$ , is rendered probable by the frequent production of butyric acid in the oxidation of conine.

Conine exists in combination with acids in all parts of the hemlock plant, but most abundantly in the fruit a little before maturity. The leaves contain a much smaller quantity, and appear to lose nearly the whole of it in drying, whereas in the fruit the quantity is little, if at all, altered by desiccation. It occurs also in the flowers. According to Walz, conine is probably also contained in the ripe seeds of fool's parsley (*Aethusa Cynapium*). According to Wagner, it appears to exist in the root of *Imperatoria*. In all these plants it exists in combination with acids, and must therefore be separated by the action of a stronger base. It then distils over easily with vapour of water.

*Preparation.*—1. The seeds of hemlock are distilled with carbonate of potassium or slaked lime, and the yellowish distillate, upon which oily drops float, is neutralised with sulphuric acid and evaporated: it then becomes red, violet, and lastly brown, and deposits brown resinous flakes, which are separated by filtration. The filtrate is evaporated to the consistence of thick syrup, and the residue is treated with a mixture of three parts absolute alcohol and one part ether, as long as it continues to grow turbid. A precipitate of sulphate of ammonia is thus formed, from which the liquid is filtered and then distilled; and the residue is heated in a water-bath and repeatedly moistened with water, until no more alcoholic vapours are perceptible. On cooling, the mass is found to contain a number of micaceous laminae, which cannot be separated. The whole is, therefore, distilled with potash in a chloride-of-calcium bath, whereupon a clear yellowish oil first passes over, containing alcohol (probably from ethyl-sulphate of potassium), and smelling strongly of conine. If this product is rendered turbid by mixture with the following distillate, the receiver must be changed, and the distillation continued till the residue is almost dry, when it is again to be mixed with caustic potash and water, and distilled as long as conine continues to pass over. The distillate, consisting of a watery liquid and oily conine, which still contains water in solution (for which reason it becomes turbid when heated), is mixed with chloride of calcium as long as the latter continues to absorb water, and then distilled; ammonia is then evolved, and there remains a brown resinous residue. The distillate is again treated with chloride of calcium and distilled in a sand-bath, and the product, which is almost colourless, is rectified alone; it then leaves a small resinous residue. 6 lbs. of fresh green, unripe seeds, or 9 lbs. dry ripe seeds, yield 1 oz. conine. (Geiger.)

2. The ripe seeds are exhausted with alcohol, the alcohol is distilled off, and the residual syrup is mixed with an equal volume of water and a little hydrate of potassium, and distilled in a chloride-of-calcium bath. (Christison.)

3. When the fresh flowers (or seeds) of hemlock are exhausted with hot water to which a little sulphuric acid has been added, and the extract supersaturated with lime or hydrate of potassium and distilled as rapidly as possible, a strongly alkaline distillate, containing ammonia, conine, and conhydrine passes over. The distillate is neutralised with sulphuric acid, evaporated on a water-bath to a thick syrupy consistence, and then treated with absolute alcohol, which precipitates sulphate of ammonia. The solution is removed from the deposit and placed on a water-bath, in order to evaporate off the alcohol; the residue is allowed to cool, then strongly supersaturated with concentrated potash and mixed with ether, the whole being shaken for a considerable time. The brownish red ethereal solution thus obtained is separated from the aqueous solution and evaporated on a water-bath, till the ether is completely driven off; it is finally heated to  $100^{\circ}\text{C}$ ., and then distilled in a stream of hydrogen, at a very slowly increasing temperature, in an oil-bath. Conine rendered impure by a little water and ether, first passes over, and afterwards colourless oily conine, which may easily be purified by neutralising with hydrochloric acid, pouring off the mother-liquor from the crystals of hydrochlorate of conine, and recrystallising the salt from alcohol. Conhydrine remains in the retort, and, on heating, sublimes in the upper part and neck of the retort in crystalline laminae; if very slowly heated, it sublimes at  $150^{\circ}\text{C}$ ., otherwise between  $190^{\circ}$  and  $210^{\circ}$ . (Wertheim.)

*Purification.*—Conine, obtained by Geiger's process, may still contain ammonia. To remove this impurity, the product is shaken in a long glass tube with water, and after a few hours, the conine is decanted off. The wash-water becomes milky on being shaken up with chlorine-water, but does not evolve nitrogen gas if free from ammonia (Boutron-Charlard and Henry). The ammonia is removed by placing the conine in vacuo over sulphuric acid; the evolution of gas-bubbles causes ebullition (Liebig). If the conine contains water, it is mixed with fused hydrate of potassium: the conine



then separates out, after a time, in an oily stratum, which is removed and rectified alone. Commercial chloride of calcium cannot be used for this purpose, as it generally contains alumina.

*Properties.*—Conine is a limpid oily liquid of specific gravity 0.89 (Geiger), 0.878 (Blyth). It boils at 168°—171° C. (Blyth); at 187.5° C. (Geiger); 189° C. (Christison); 212° C. (Ortigosa); and when carefully but rapidly heated, distils almost without decomposition (Geiger). It volatilises in vacuo at ordinary temperatures, and distils without residue (Liebig, Ortigosa). It may be carried over with vapour of water at 100° C., but not without slight decomposition. It has a highly penetrating, repulsive, peculiar, and suffocating odour, like that of tobacco, and somewhat resembling that of hemlock; at a distance, and in small quantity, it smells like mice; if closely inhaled, it attacks the head and provokes tears (Geiger). Its taste is sharp, repulsive, and persistent, like that of tobacco. It is a violent poison, small quantities of it rapidly causing death, attended with tetanus. When outwardly applied, it does not dilate the pupil, even if introduced into the eye itself (Geiger). (On the action of conine, see Christison, *J. Pharm.* xxii. 413; *J. Chim. méd.* xii. 461. Kuhlmann, *N. Br. Arch.* xxiii. 38.) It has a strong alkaline reaction, but only in the presence of water (Geiger). The alkaline reaction disappears from turmeric paper on application of heat, and slowly from litmus paper. (Blyth.)

The composition of conine is as follows:

			By calculation.	Ortigosa.	Blyth.
Carbon	8 atoms	.	96	76.80	74.59
Hydrogen	15 "	.	15	12.00	12.05
Nitrogen	1 "	.	14	11.20	13.06
			125	100.00	

Conine is slightly soluble in water at ordinary temperatures; it is also capable of dissolving one-third of its weight of water, and at low temperatures an equal weight; if it be then heated, it becomes turbid, from separation of water (Geiger). It is very soluble in alcohol, and when dissolved in 4 pts. of alcohol, may be mixed in all proportions with water. It is easily soluble in ether, in oils, both fixed and volatile, and in acetone.

Conine dissolves sulphur in large quantity, forming a dark orange-coloured solution, which yields crystals of sulphur by evaporation. It is slightly soluble in sulphide of carbon. It does not appear to dissolve phosphorus.

*Decompositions.*—1. Conine is very inflammable, and burns with a bright smoky flame, like volatile oils, leaving only a small residue of carbon. (Geiger.)

2. When kept from the air, conine remains colourless, but, on exposure to the air, it rapidly turns yellow, brown, and viscid, and becomes less soluble in water. The aqueous or alcoholic solution undergoes the same decomposition, especially if the conine is impure; both rapidly turn brown, while the aqueous solution becomes turbid, and deposits resinous flakes (Geiger). In the decomposition of conine by the air, resin is formed and ammonia evolved (Christison). Conine, placed in a shallow dish, and exposed to the action of oxygen for some weeks, turns dark red, becomes thicker, and is finally converted into a stringy resinous mass, which smells strongly of conine, and has an alkaline reaction. This resin dissolves in strong hydrochloric acid, and is precipitated by carbonate of potassium. If this operation be repeated, and the product washed with water, a resin is obtained which is free from conine, smells of butyric acid when burnt or exposed to moist air, and contains nitrogen. (Blyth.)

3. On distilling conine, a portion is always decomposed, ammonia being evolved and a resin formed. The purer the conine, the less decomposition takes place. Heated for some time to a temperature near its boiling point, it is much more decomposed than when it is rapidly heated to boiling, in which case the greater part distils over unchanged; ammonia and a resin are formed, and perhaps also carbonic and acetic acids (Geiger). Moist conine, evaporated in vacuo over substances which attract moisture, leaves a resinous pitchy residue (Charlard and Henry, *Ann. Ch. Phys.* lxi. 337). Moist conine leaves a resin on distillation; the dry substance does not (Ortigosa, *Ann. Ch. Pharm.* xlii. 513). When conine is heated above 172° C., the boiling point rapidly rises, decomposition takes place, and white fumes are evolved. (Blyth.)

4. In the oxidation of conine, butyric acid is generally formed, as when conine is boiled with nitric acid (a resin is formed at the same time, which is precipitated from the solution by potash on cooling); also on evaporating hydrobromate of conine in vacuo with a slight excess of bromine, or by evaporating sulphate of conine to dryness, and by treating conine with acid chromate of potassium and sulphuric acid (Blyth). An odour of butyric acid is perceptible during the evaporation of the platinum- or mercury-salts of conine, and of its basic substitution-products (v. Planta and Kekulé). Conine reduces silver-salts. (Ortigosa.)



5. When conine is neutralised with *dilute mineral acids*, it is not decomposed by spontaneous evaporation, but if evaporated with the aid of heat, its solution becomes dark, and a salt of ammonia and a resin are formed. The same reaction is produced, even in the cold, by an excess of acid, or by *acetic or tartaric acid*. (Geiger.)

6. Alcoholic tincture of *iodine* acts violently upon moist conine, the solution becoming turbid and yellow for a few moments, and then colourless, and ultimately drying up to an uncrystallisable mass (Geiger.) A weak tincture of iodine added drop by drop to alcoholic conine, produces a dark brown precipitate, which dissolves and forms a colourless liquid. When tincture of iodine is added as long as the liquid remains colourless (if an excess of iodine is added, a different decomposition takes place), and the solution evaporated in vacuo, there remains a brownish mother-liquor, containing crystals of a similar form to those obtained by the action of bromine upon conine; they are easily soluble in water, alcohol, and ether (Blyth). Anhydrous conine becomes heated in contact with iodine, and forms thick white fumes and a readily fusible mass, which is at first blood-red, and afterwards turns olive-green; this body dissolves in water, forming a nearly colourless solution, and depositing a thick black resin. (Geiger.)

7. When conine (distilled at 169° C.) is exposed to vapour of *bromine*, it immediately solidifies into a mass of crystalline needles. If too much bromine is used, the chief product is a gummy mass; if conine is employed which distilled over below 168°, a red liquid is formed. The purer the conine, the more abundant is the formation of crystals. Conine which has passed over between 98° and 136° does not at first form any crystals with bromine, and when evaporated in vacuo, becomes dark red, or, if more bromine is added, black. This product, dissolved in water, boiled with animal charcoal, then filtered and evaporated in vacuo over sulphuric acid, yields transparent colourless needles and a brown mother-liquor. The crystals, after washing with ether, contain 48.52 per cent. C, and 8.98 H; they are readily soluble in water and in alcohol, but much less in ether; when purified by treating them with ether, and recrystallised from water or from alcohol, they form needles which are permanent in the air and melt into an oil at about 100° C., giving off a little conine vapour. On cooling, the oil solidifies into a striated mass. (Blyth.)

8. Anhydrous conine, acted upon by *chlorine gas*, gives off dense white fumes, becomes hot and thick, and forms a dark brown mass, which has a peculiar odour, something like that of chlorine, but not like that of conine, and when suspended in water and treated with caustic soda, diffuses an odour of conine and turpentine. With hydrated conine, chlorine gas produces a whitish turbidity, separation of oil drops, and a smell of chloride of nitrogen; if potash be then added, an odour of conine is evolved (Geiger). Moist conine, free from ammonia, does not evolve nitrogen when shaken with chlorine-water (Charlard and Henry). When chlorine gas is passed over conine which has distilled at 130° C., the conine becomes hot, assumes a dark red colour, and emits heavy white vapours which smell somewhat like oil of lemon. If the action of the chlorine be continued and the oil cooled, it becomes colourless again and thicker, ceases to evolve white vapours, and becomes covered with white crystals, into which it is completely converted after the chlorine has been passed over it for a long time. The crystals are like those formed by the action of bromine, and are very volatile. If stirred up with water, they readily dissolve; they are very soluble in alcohol and ether, from which they crystallise.

9. Anhydrous conine poured upon dry *chromic acid*, takes fire immediately. (Hofmann, Ann. Ch. Pharm. xlvii. 85.)

10. *Phosphomolybdic acid* (obtained by precipitating molybdate of ammonium with common phosphate of sodium, evaporating the solution to dryness, igniting till the ammonia is driven off, and dissolving the residue in water containing nitric acid) forms with conine and its salts, a bright yellow bulky precipitate. The precipitate is scarcely soluble at ordinary temperatures in water, dilute acids (with the exception of phosphoric acid), alcohol, or ether; it is however readily taken up by the carbonates, borates, and phosphates of the alkalis, and decomposed, though with difficulty, with separation of conine, by the alkaline earths and their carbonates, as well as by the oxides of lead and silver and their carbonates. (Sonnenschein, Ann. Ch. Pharm. cv. 45.)

11. Conine is rapidly attacked by *bromide of ethyl*, and forms a crystalline product (Hofmann, Ann. Ch. Pharm. lxxiv. 175; lxxix. 34). Commercial conine mixes with iodide of ethyl, and forms at first a clear liquid; but a reaction quickly takes place, whereby a brown oil is formed, which sinks to the bottom of the vessel. If the mixture is heated in a sealed tube to 100° C., till the stratum of ether at the bottom no longer decreases, there is formed, if the conine is pure, a viscid oil (hydriodate of ethyl-conine); but if the conine contains methyl-conine, there is formed, besides hydriodate of ethyl-conine, the hydriodate of ethyl-methyl-conine, which solidifies in part immediately, and completely on cooling. (v. Planta and Kekulé.)

12. *Cyanate of ethyl* dissolves conine, with evolution of heat, forming a compound urea, the crystallisation of which causes the mixture to solidify on cooling. (Wurtz.)



**SALTS OF CONINE.**—Conine is a strong base, and neutralises acids completely; forming salts in which 1 at. conine is united with 1 at. of a monobasic acid, 2 at. conine with 1 at. of a dibasic acid, &c. These salts may be obtained in the solid state by leaving their solutions to evaporate in vacuo, but they are difficult to crystallise. They dissolve easily in water, in alcohol, and in a mixture of alcohol and ether, but are insoluble in pure ether. Many of them are deliquescent. They have a disagreeable, bitter, and acrid taste, like that of tobacco. In the dry state they are odourless, but the aqueous solutions always smell of conine. They are decomposed by heat.

The aqueous solutions of conine-salts form, with *iodine-solution*, a saffron-coloured precipitate, which soon redissolves. They yield flocculent precipitates with *tincture of galls* and *dichloride of platinum*. With *alkalis*, they give off the peculiar odour of conine; and when shaken up with a solution of *sulphate of magnesium*, they form a crystalline salt. The solutions, when exposed to the air, gradually change, from the decomposition of the conine, acquiring a beautiful red or violet colour, which afterwards changes to green or dark blue, and disappears again on addition of alkalis; if quite neutral, they often become yellow or brownish. A much more rapid decomposition takes place when the solution of a conine-salt is evaporated by heat and in contact with the air, the conine appearing to suffer the same alteration as when exposed to the air in the free state; the solutions become brown, and deposit brown flocks, and if an alkali be then added, ammonia and conine are set free, and a dark-brown, bitter, resinous substance is separated, which does not exert any poisonous action.

According to Geiger, conine-salts are less poisonous than the base itself; according to Christison's experiments, on the contrary, the poisonous action of conine is greatly intensified by neutralisation with acids. Five grains of conine, neutralised with hydrochloric acid, and introduced into the vein of a small dog, killed it in a few seconds.

*Acetate of Conine* dries up, by spontaneous evaporation, to a brown varnish-like mass, which dissolves in water.

*Hydrochlorate of Conine*,  $C^8H^{13}N.HCl$ .—Hydrochloric acid gas colours dry conine red and then blue. When conine is placed under the receiver of an air-pump, beside a vessel containing fuming hydrochloric acid, crystals of the hydrochlorate are formed in both vessels, having the form of beautiful, colourless, transparent laminae (Liebig). According to Wertheim (Ann. Ch. Pharm. c. 335), conine evaporated with hydrochloric acid, yields rhombic crystals from 2 to 4 millimetres long, and having a rather strong fatty lustre; they are easily purified by recrystallisation from alcohol. The salt dissolves easily in water, and becomes moist in contact with the air. If the solution be left to evaporate in contact with the air, the salt again crystallises in laminae, but turns brown from decomposition.

*Chloroplatinate of Conine*,  $C^8H^{13}N.HCl.PtCl_2$ , obtained by mixing an alcoholic solution of conine with dichloride of platinum, and evaporating in vacuo over oil of vitriol, is an orange-yellow crystalline powder, soluble in water and in boiling alcohol, insoluble in ether-alcohol (Ortigas); decomposed at  $100^\circ C$ .

*Nitrate of Conine* is obtained, by spontaneous evaporation, as a brown deliquescent mass, having the consistence of an extract, mixed with small needles and crystalline granules.

*Sulphate of Conine*.—Conine, saturated with dilute sulphuric acid, assumes a brownish colour on evaporation, and leaves a thick gummy mass, with traces of crystallisation. According to Charlard and Henry, the salt is crystallisable, deliquescent, and dissolves in all proportions in alcohol. Potash separates the conine. If the evaporation be carried too far, decomposition takes place, and the odour of butyric acid becomes perceptible. Sulphate of conine forms with *sulphate of aluminium*, a double salt which crystallises in octahedrons (conine-alum).

*Tartrate of Conine*.—The solution, left to evaporate in the air, becomes turbid, acquires a green and then a brown colour, and leaves an extract-like mass, containing small granular crystals. On heating the mass with water, a few brown flakes remain undissolved.

Conine forms crystallisable salts with iodic, oxalic, and phosphoric acids.

#### *Substitution-derivatives of Conine.*

Conine is a secondary monamine,  $N.H.(C^2H^4)^2$ , or  $N.H.(C^2H^7)^2$ , containing only one atom of replaceable hydrogen: for when it is treated with iodide of ethyl, hydriodic acid is formed, and the ethyl takes the place of 1 at. hydrogen in the base, the product being *hydriodate of ethyl-conine* ( $N.C^2H^5.C^2H^4$ ).HI; but on treating ethylconine with iodide of ethyl, no further substitution takes place, but the two bodies unite directly, forming *iodethylate of ethylconine* ( $N.C^2H^5.C^2H^4$ ). $C^2H^5I$ , or rather *iodide of diethylconinium* [ $N.(C^2H^5)^2.C^2H^4$ ].I.

**METHYL-CONINE.**  $C^8H^{11}N = N.CH^3.C^8H^{11}$ .—This base is often contained in commercial conine. It is also produced by the action of heat on ethyl-methyl-conine. It is a colourless oil, smelling like conine, lighter than water, and sparingly soluble in water, imparting, however, a strong alkaline reaction. Iodide of ethyl converts it into iodide of ethyl-methyl-coninium.

**ETHYL-CONINE.**  $C^{10}H^{19}N = N.C^2H^5.C^8H^{11}$ . (v. Planta and Kekulé, Ann. Ch. Pharm. lxxxix. 131.)—The hydriodate of this base is obtained by heating conine with iodide of ethyl in a sealed tube to  $100^\circ C.$  for about half an hour; and by dissolving the product in water, removing the excess of iodide of ethyl by decantation, and gently heating the solution with caustic potash, ethyl-conine separates, and may be rectified in a current of hydrogen after being dried over fragments of chloride of calcium and solid potash.

Ethyl-conine is a volatile, almost colourless, strongly refracting oil, lighter than water, smelling like conine, partially decomposed by distillation. Iodide of ethyl converts it into iodide of diethyl-coninium.

Ethyl-conine is sparingly soluble in water, but dissolves readily in acids, with considerable evolution of heat. Its salts do not crystallise by evaporation.

The *hydrobromate* and *hydriodate* are uncrystallisable. The *hydrochlorate* is obtained, as a mass of white deliquescent crystals, by leaving anhydrous ethyl-conine under an exhausted receiver beside a vessel containing fuming hydrochloric acid. The *chloro-aurate* is precipitated as a yellowish oil which solidifies and crystallises; from a hot dilute solution it sometimes separates in beautiful yellow crystals. The *chloromercurate* is obtained by precipitation, as a white resinous substance, which melts in the liquid at the boiling heat, and if dilute solutions are used, separates in rhomboidal tablets. The *chloroplatinate*,  $C^{10}H^{19}N.HClPtCl^2$ , is a yellow crystalline powder easily soluble in water and in alcohol.

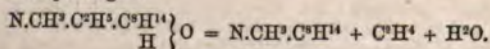
**DIETHYL-CONINIUM,**  $C^{12}H^{24}N = N.(C^2H^5)^2.C^8H^{11}$ . (v. Planta and Kekulé, Ann. Ch. Pharm. lxxxix. 146.)—Known only in combination. The iodide,  $C^{12}H^{24}NI$ , is obtained by the action of iodide of ethyl on ethyl-conine in the cold. This mixture, left to itself for 12 hours, forms a crystalline mass; and on heating this product in a sealed tube to  $100^\circ C.$ , the iodide of diethyl-coninium melts to a liquid which floats on the iodide of ethyl. The crystals are softer than those of ethyl-methyl-coninium, dissolve easily in water and alcohol, less readily in ether.

The *hydrate* is obtained in solution by decomposing the iodide with oxide of silver. The solution is inodorous, has a bitter taste, and strong alkaline reaction.

The *chloride*, obtained by saturating the base with hydrochloric acid, forms, with *chloride of mercury*, a white flocculent precipitate, which melts when heated, and separates from the hot solution after some time in microscopic crystals; with *trichloride of gold*, a sulphur-yellow semi-fluid precipitate which dissolves when heated, and separates on cooling in oily drops which become solid and crystalline; and with *dichloride of platinum*, on evaporation, a crystalline salt containing  $C^{12}H^{24}N.ClPtCl^2$ .

**ETHYL-METHYL-CONINIUM,**  $C^{11}H^{22}N = N.CH^3.C^2H^5.C^8H^{11}$ . (v. Planta and Kekulé, Ann. Ch. Pharm. lxxxix. 135.)—This base also is known only in combination. The *iodide* is produced by the action of iodide of ethyl on methyl-conine. When commercial conine, containing the latter compound (ii. 5), is treated with iodide of ethyl, it yields, besides the syrupy hydriodate of ethyl-conine, crystals of the iodide of ethyl-methyl-coninium. The reaction takes place even in the cold, and is completed in a few minutes at the heat of the water-bath. On dissolving the product in water, removing the mass of iodide of ethyl, and adding caustic potash, a brown oil separates which divides into two layers, the upper, which consists of ethyl-conine, remaining liquid, while the lower, consisting of iodide of ethyl-methyl-coninium, separates in splendid needles, which may be purified by washing with ether containing a little alcohol.

*Hydrate of Ethyl-methyl-coninium* is obtained in solution by decomposing the iodide with recently precipitated oxide of silver. The solution is colourless, inodorous, very bitter, strongly alkaline, and when concentrated acts on the skin like caustic potash. It absorbs carbonic acid quickly from the air. It may be boiled without decomposition, but when concentrated and distilled, it is resolved in methyl-conine, water, and ethylene gas:



Heated in a sealed tube with iodide of ethyl, it is converted into alcohol and iodide of ethyl-methyl-coninium.



The *chloride, sulphate, nitrate, carbonate, oxalate, and acetate* of ethyl-methyl-conium are crystallisable, very soluble in water, and, for the most part, deliquescent.

The *iodide*,  $C^{11}H^{22}NI$ , forms colourless needles very soluble in water and in alcohol, insoluble in ether and in alkaline liquids. It may be boiled with caustic potash without decomposition.

*Chloro-aurate*,  $C^{11}H^{22}NClAuCl^3$ .—Precipitated by chloride of gold from a solution of the base in hydrochloric acid, in yellow flakes which soon become crystalline. From hot solutions, the salt is deposited in fine needles on cooling. The dry salt melts below  $100^{\circ}C$ . (Gold, by analysis, 38.67 per cent., by calculation 38.86 per cent.)

*Chloro-mercurate*,  $C^{11}H^{22}NCl_2HgCl$ .—White crystalline precipitate, moderately soluble in water, alcohol, and ether. Gives by analysis, 59.16 per cent. Hg, and 24.63 Cl, the formula requiring 59.03 Hg, and 24.45 Cl. When heated with water, it melts and dissolves, and the solution, on standing, deposits another salt containing  $C^{11}H^{22}NCl_2HgCl$ . (Analysis, 14.26 per cent. C, 2.70 H, and 55.78 Hg; calculation, 14.98 C, 2.60 H, and 56.75 Hg.)

*Chloroplatinate*,  $C^{11}H^{22}NCl.PtCl^3$ .—Precipitated as a yellow crystalline powder, or from dilute solutions, gradually, in fine octahedrons. It is sparingly soluble in cold water, more soluble in boiling water, insoluble in alcohol and ether. (Mean of analyses, 35.49 per cent. C, 6.54 H, and 26.43 Pt; calculation, 35.37 C, 5.86 H, and 26.45 Pt.)

**CONISTONITE.** A name given by R. P. Greg (Sill. Am. J. xvii. 333) to a hydrated oxalate of calcium in crystals of the trimetric system, from Coniston in Cumberland; afterwards, however, found not to be a natural mineral (*ibid.* xxii. 262).

**CONITE**, or *Konite*. Compact dolomite.

**CONIUM MACULATUM.** *Hemlock*.—This very poisonous plant contains the two alkaloids, conine and conhydrine. It loses its activity by drying, and, according to Müller, by keeping for twelve months. The extract loses its activity with equal facility, the alcoholic sooner than the aqueous extract. According to Landerer, the green parts of the plant contain also a small quantity of an extremely intoxicating oil. 100 pts. of the dry leaves contain, according to Wrightson (Pharm. J. Trans. v. 40), 6.8 pts. nitrogen, and 12.8 ash, consisting, after deduction of carbonic acid, sand, and charcoal, of 21.7 per cent. potash, 9.6 soda, 14.9 lime, 8.3 magnesia, 2.6 silica, 5.9 sulphate of calcium, 16.7 phosphate of calcium, 3.5 ferric phosphate, and 16.6 chloride of sodium.

**CONJUGATED COMPOUNDS.** *Copulated compounds. Corps conjugués ou copulés. Gepaarte Verbindungen.*—These terms, the meaning of which has never been very clearly defined, were first introduced into organic chemistry by Gerhardt, in 1839. He had observed that certain acids, especially sulphuric acid, produce, by their action on organic bodies, peculiar compounds in which the characteristic properties of the original substances are no longer perceptible; benzoic acid, for example, is converted by sulphuric acid into sulpho-benzoic acid, a compound in which the presence of sulphuric acid cannot be detected by barium-salts. This kind of union was called by Gerhardt copulation (*accomplissement*); the product, a copulated compound (*sel copulé*), and the organic body which united with the sulphuric acid, was called the copula (*copule, Paarung*).

To explain the formation and properties of these substances, Gerhardt supposed that the action of sulphuric acid and similar acids on organic bodies may take place in two ways. Either the acting acid loses its saturating power, in which case the product is formed by substitution, *e.g.* *sulphobenzide*,  $\frac{C^{12}H^6}{SO^2}$  from *benzole*,  $C^{12}H^6$ , by the substitution of  $SO^2$  for 1 at. H; or the acting acid retains its saturating capacity, in which combination takes place by copulation. In many cases both these actions were supposed to take place together; thus the formation and composition of sulpho-benzoic acid (anhydrous) were represented by the formula  $\frac{C^{12}H^6}{SO^2}O^2 + SO^2$ .

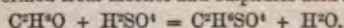
Similar views regarding the constitution of such acids were put forth about the same time by Dumas and Piria, who designated them as "conjugated acids." Berzelius also adopted the terms copulated and conjugated, but applied them in a different sense, namely, to designate compounds which he could not regard as formed by the union of elements or compound radicles in opposite electrical states; thus water, metallic oxides, and the corresponding oxides of organic radicles, were supposed to be capable of uniting with acids, or electro-negative bodies, in the ordinary way; but the union of all other

bodies was called copulation. Thus acetic acid,  $C^2H^3O^2$ , was regarded as oxalic acid,  $C^2O^2$ , copulated with methyl,  $C^2H^3$ ; trichloroacetic acid,  $C^2Cl^3O^2$ , as oxalic acid,  $C^2O^2$  copulated with sesquichloride of carbon,  $C^2Cl^3$ . A copulated compound was defined as a compound of an active substance (*e. g.* the oxalic acid in the compounds just mentioned) with a passive substance or copula. Substitution (of Cl for H for example) was supposed to take place only in the latter. These views of Berzelius have clearly no connection with those previously mentioned. Gerhardt in fact protested against this use of terms which he had introduced in a different sense, and, at the same time, defined conjugated compounds as bodies produced by the substitution of "residues" (or compound radicles) for elementary bodies,—this definition including the amides, compound ethers, nitro-substitution compounds, as well as the compounds formed by the action of sulphuric, phosphoric, and other polybasic acids on hydro-carbons and organic acids.

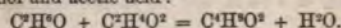
In a memoir on the anilides published by Laurent and Gerhardt in 1848, the following definition is given:—"We designate as conjugate compounds, all such as are formed by the direct union of two bodies, with elimination of water, and are capable of reproducing the original bodies by again taking up the elements of water."

The following are examples:

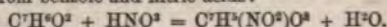
Ethyl-sulphuric acid, formed from alcohol and sulphuric acid:



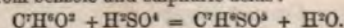
Acetic ether from alcohol and acetic acid:



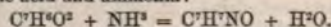
Nitro-benzoic acid, from benzoic and nitric acids:



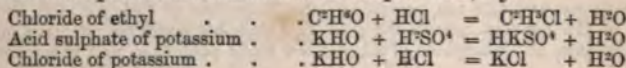
Sulpho-benzoic acid, from benzoic and sulphuric acids:



Benzamide, from benzoic acid and ammonia:



It is easy to see, however, that on this definition nearly all chemical compounds might be regarded as conjugated: for the mode of action just illustrated is precisely that which takes place in the formation of the simplest salts, *e. g.*:



More recently (in his *Traité de Chimie Organique*, 1853-56) Gerhardt, while he admits that in a certain sense all organic compounds may be regarded as conjugated, nevertheless restricts the actual use of the term to certain groups of bodies, without, however, distinctly stating what they are. He no longer applies it to the ethers, either acid or neutral, or to the amides; but includes among conjugated compounds the amic acids, and compounds formed by the substitution of bromine, chlorine, or nitryl, for hydrogen. The idea of a conjugated compound he explains as follows:—

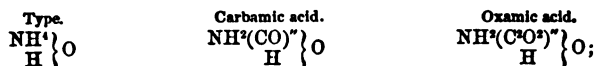
"To connect together two or more systems of double decomposition of one and the same body, it is often advantageous to represent its composition by a conjugated radicle, that is to say, a radicle made up of several radicles, each of which represents one such system of decomposition. We must regard as conjugated the radicle of every body capable of being transformed, by certain very simple reactions, into compounds belonging to other radicles (*radicaux constituants*), or in other words, the radicle of every body resulting from the metamorphosis of such combinations. Thus acetyl,  $C^2H^3O$ , may be regarded as a conjugated radicle composed of carbonyl, CO, and methyl,  $CH^3$ , because acetic acid and its derivatives are capable of splitting up into compounds containing carbonyl, and others containing methyl (i. 17); and conversely, acetic acid may be produced by the action of carbonic anhydride on potassium-methyl. Similarly with the radicles of the other fatty acids; thus, formyl = CO.H; propionyl = CO. $C^2H^3$ ; butyryl = CO. $C^3H^7$ ; amyl = CO. $C^4H^9$ , &c. The same acid radicles may also be regarded as alcohol-radicles in which H<sup>2</sup> is replaced by O; thus acetyl,  $C^2H^3O$ , may be regarded as formed from ethyl,  $C^2H^5$ ; propionyl,  $C^3H^7O$ , from trityl,  $C^3H^7$ ; butyryl,  $C^4H^9O$ , from tetryl,  $C^4H^9$ ; this mode of representation corresponding to the fact that the alcohols are converted into fatty acids by oxidation."

In general, complex radicles may be regarded as conjugated either by addition or by substitution; *e. g.* tetrethylammonium,  $N(C^2H^5)^4$ , is either a compound of N with 4 at. ethyl; or it is ammonium,  $NH^4$ , in which 4 at. H are replaced by ethyl. The mode of representation by substitution is especially applicable to bodies formed by the action

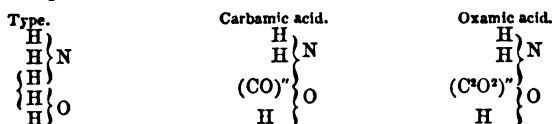
of chlorine, bromine, nitric acid, or sulphuric acid on organic bodies, and to the amides, amines, and ammonium-bases.

From these considerations—for the full development of which we must refer to *Gerhardt's Traité* (iv. 602)—it will be seen that Gerhardt ultimately gave up the idea of conjugated compounds as distinct from others, and retained the term merely for the sake of comprehending certain substances in groups, and exhibiting certain analogies in a clearer light. His formulæ, in fact, represent decompositions, the most important transformations being indicated by the radicles which appear in the typical formula: thus, when acetic acid is written,  $\begin{matrix} \text{C}^2\text{H}^1\text{O} \\ \text{H} \end{matrix} \left\{ \text{O} \right.$ , we are reminded that 1 at. of hydrogen may be exchanged for a metal or other basylous radicle, and that 1 at. O (outside the radicle) may be replaced by S, yielding thiactic acid, or by 2 at. Cl, yielding chloride of acetyl and chloride of hydrogen. In these transformations the radicle acetyl remains unaltered, and may be regarded as a simple substance; but any other transformations must affect the radicle itself, and to indicate these, the formula of acetyl must be resolved into others, in the manner above mentioned, the acetyl then appearing as a conjugate instead of as a simple radicle. (See CLASSIFICATION, i. 1017.)

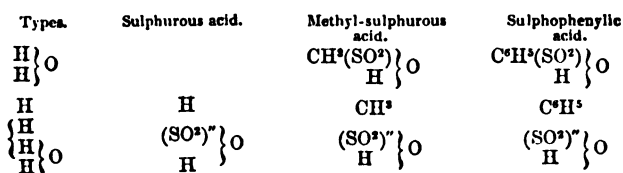
Considered in this light, conjugate radicles are merely modes of expression adopted for convenience; and it is easy to show that by the extensions of the typical mode of representation of chemical compounds which have come into use since the publication of Gerhardt's work, the use of conjugate radicles may be dispensed with altogether (see TYPES). For example, Gerhardt represents the amic acids as containing radicles of this class, and refers them to the type  $\text{H}^2\text{O}$ ; thus—



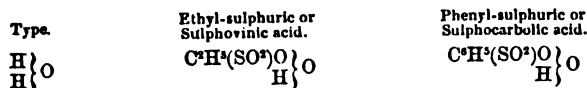
but they may also be referred to the mixed type  $\begin{matrix} \text{NH}^1 \\ \text{OH}^2 \end{matrix} \left\{ \right.$ , and then the conjugate radicles may be broken up: thus—



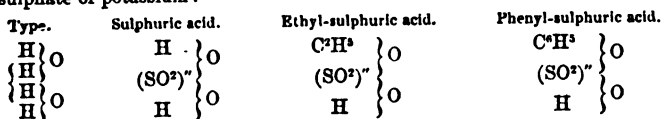
In like manner, many sulpho-acids, supposed by Gerhardt to contain conjugate radicles, because they were referred to the type  $\text{H}^2\text{O}$ , may be regarded as derived from the mixed type  $\begin{matrix} \text{H}^1\text{O} \\ \text{H}^2 \end{matrix} \left\{ \right.$  and as containing simple radicles, e.g.:



The same mode of representation may be applied to the acid ethers of dibasic acids. If they are referred to the type  $\text{H}^2\text{O}$ , they must be supposed to contain conjugate radicles:



but by referring them to the type  $\text{H}^1\text{O}^2$ , they appear as acid salts exactly analogous to acid sulphate of potassium:



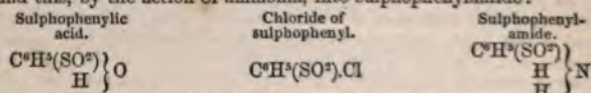
These examples are sufficient to show that the transformations of any compound, so far as they are known, may be represented by typical formulæ without the assumption



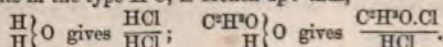
of conjugate radicles. Still the use of these radicles is often convenient, inasmuch as it affords typical formulae of comparatively simple structure, and such as bring prominently into view a certain set of reactions, which may be the especial object of consideration. But it applies equally well to all classes of compounds, excepting of course the very simplest; and the compounds to which the term conjugate has been and still is by some chemists most frequently applied, are not distinguished by any essential characters from those which are commonly assumed to be of simple constitution.

We must not, however, omit to notice that there are a few compounds, produced by the action of sulphuric acid on organic bodies,—the very class, indeed, to which the term conjugate was originally applied,—which are still supposed, by some chemists, to possess peculiar properties entitling them to the name.

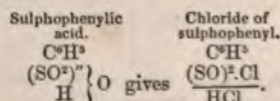
One characteristic of a true conjugated acid, is said to be the comparatively greater permanence of the compound radicle which it contains, and the power possessed by that radicle of passing from one type to another without decomposition. Thus, sulphophenylic acid is transformed by pentachloride of phosphorus into chloride of sulphophenyl, and this, by the action of ammonia, into sulphophenylamide:



Here the radicle  $\text{C}^6\text{H}_5(\text{SO}^2)$ , which is found in all the three compounds, is said to be conjugated. The formation of the chloride from the acid may, however, be shown to take place quite in the usual way, without assuming any peculiar fixity in this radicle. The action of chloride of phosphorus on acids and other oxides is known to consist in the replacement of O, in the type  $\text{H}^2\text{O}$ , by  $\text{Cl}^2$ , the result being the formation of two separate chlorides, because the bond which held together the two atoms of hydrogen, or their equivalents in the type  $\text{H}^2\text{O}$ , is broken up: thus,

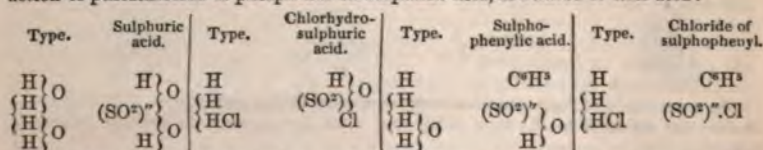


In like manner, if we represent sulphophenylic acid by a formula modelled on the mixed type  $\left\{\begin{smallmatrix} \text{H}^2\text{O} \\ \text{H}^2 \end{smallmatrix}\right\}$ , we find that

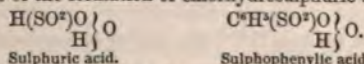


The chloride belongs to the mixed type  $\left\{\begin{smallmatrix} \text{H}^2 \\ \text{HCl} \end{smallmatrix}\right\}$ , the two molecules  $\text{H}^2$  and  $\text{HCl}$  being held together by the radicle  $\text{SO}^2$ , just as the two molecules  $\text{H}^2$  and  $\text{H}^2\text{O}$  were in the original acid.

In fact, chloride of sulphophenyl is related to sulphophenylic acid in exactly the same manner as chlorhydrosulphuric acid ( $\text{SO}^2\text{HCl}$ ), the compound formed by the action of pentachloride of phosphorus on sulphuric acid, is related to that acid:



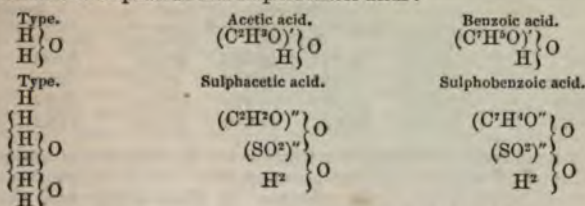
If sulphophenylic acid is to be regarded as conjugated, on account of the formation of chloride of sulphophenyl, sulphuric acid ought likewise to be regarded as a conjugated acid, on account of the formation of chlorhydrosulphuric acid:



Chlorhydrosulphuric acid would then be regarded as the chloride of the same radicle, namely,  $\text{H}(\text{SO}^2)\text{O.Cl}$ ; in fact, when treated with water, it reproduces sulphuric acid, just as chloride of sulphophenyl reproduces sulphophenylic acid. (Kekulé.)

Another class of acids to which the term conjugate is still sometimes applied, includes those which result from a peculiar action of sulphuric acid, especially of the fuming acid, on certain organic bodies,—the change consisting in the abstraction of an atom of hydrogen from the radicle of the compound, which radicle accordingly undergoes an alteration of atomicity, becoming, for example, diatomic instead of monatomic.

This change may, however, be easily represented by means of mixed types, as in the following formulae of sulphacetic and sulphobenzoic acids:



These sulpho-acids are formed from acetic and benzoic acid in the same manner as isethionic acid,  $\begin{array}{c} (\text{C}^2\text{H}^4)'' \\ (\text{SO}^2)'' \\ \text{H}^2 \end{array} \left\{ \begin{array}{c} \text{O} \\ \text{O} \\ \text{O} \end{array} \right.$ , from alcohol,  $\begin{array}{c} \text{C}^2\text{H}^3 \\ \text{H} \end{array} \left\{ \begin{array}{c} \text{O} \\ \text{O} \end{array} \right.$ . Now this last acid may be formed

by the action of boiling water on sulphate of carbyl,  $\text{C}^2\text{H}^3\text{S}^2\text{O}^6$ , or  $\begin{array}{c} (\text{C}^2\text{H}^4)'' \\ (\text{SO}^2)'' \\ (\text{SO}^2)'' \end{array} \left\{ \begin{array}{c} \text{O} \\ \text{O} \\ \text{O} \end{array} \right.$ , which is itself a product of the action of sulphuric anhydride upon ethylene  $\text{C}^2\text{H}^4$ . In this last mode of formation there is no alteration of the radicle; consequently, if such alteration were supposed to necessitate the representation of the resulting compound by a formula containing a conjugate radicle, *e. g.* sulphacetic acid, by  $\begin{array}{c} \text{C}^2\text{H}^3\text{O}(\text{SO}^2) \\ \text{H} \end{array} \left\{ \begin{array}{c} \text{O} \\ \text{O} \end{array} \right.$ , and isethionic

acid, by  $\begin{array}{c} \text{C}^2\text{H}^4(\text{SO}^2) \\ \text{H} \end{array} \left\{ \begin{array}{c} \text{O} \\ \text{O} \end{array} \right.$ , it would follow that the last-mentioned acid might be regarded as conjugated or non-conjugated, according as it was formed from alcohol or from olefiant gas.

From all these considerations it follows that there is no case in which the use of conjugate radicles is a matter of necessity, the use of a radicle or of a type of greater or less complexity being in all cases a matter of convenience, and determined by the particular kind of chemical transformation which the formula is intended to represent. It would be well, therefore, if the idea of conjugation, as denoting any peculiar mode of chemical combination, were altogether banished from the science (Kekulé, *Lehrbuch der Organischen Chemie*, 1859, i. 192).—On the history of conjugate compounds, see also Limpricht and v. Uslar, *Ann. Ch. Pharm.* cii. 139; Mendius, *ibid.* ciii. 39; Kekulé, *ibid.* civ. 129; cvi. 129; Limpricht, *ibid.* civ. 177; also the articles CLASSIFICATION, RADICLES, SUBSTITUTION, and TYPES, in this Dictionary.

**CONNECTIVE TISSUE.** *Bindgewebe.*—This term is applied to a tissue chemically allied to cartilage, though of a simpler character, and comprises, not merely the porous soft cellular substance, characterised by the readiness with which it may be filled with air, which connects together the various organs and tissues of the animal organism, and was formerly called *cellular tissue*, but also those morphological elements which constitute the solid basis of many of the animal membranes and ligaments. The tissue which connects the organs one with another, forming a network of variously sized meshes composed of long slender fibres (of 0.0003–0.0005" diameter), for the most part united in bundles, is called *amorphous* (Henle), or *loose*, *areolar connective tissue* (Kölliker). This tissue gradually passes into a more solid variety distinguished by the epithet *formed* (Henle), or *compact* (Kölliker), which forms the basis of the tendons and ligaments, the fibrous membranes and muscular fasciæ, the envelopes of many soft organs (the *dura mater*, *neurolemma*, &c.), the serous and synovial membranes, the coats of the veins, the so-called vascular membranes, (*pia mater*, *choroidea*, &c.), the interarticular cartilages, &c.

The true connective tissue is, however, constantly mixed with vessels, nerves, fat-cells, elastic fibres, and frequently also with unstriated muscular fibres, which cannot be mechanically separated from it, so that its chemical examination is a matter of some difficulty; but from the analysis of those organs, such as the tendons, in which it is mixed with the smallest amount of these morphological elements, it appears to be identical in composition with gelatin.

Connective tissue immersed in boiling water contracts somewhat at first, but soon swells up like a jelly, and dissolves on prolonged boiling, yielding a solution of gelatin. If the water contains an acid or alkali in solution, the transformation is effected much more quickly.

The change which here takes place is rather physical than chemical: for the connective, and indeed all the gelatinising tissues, appear to have essentially the same composition as gelatin itself, as may be seen from the following analyses by Scherer



(Ann. Ch. Pharm. lx. 46-49) and Mulder (*Vers. einer allgem. physiol. Chem.* Braun-schweig, 1844—51, p. 333.)

	Scherer.			Mulder.	
	Isinglass.	Tendons.	Sclerotica.	Stag's horn.	Isinglass.
Carbon . . .	50-557	50-774	49-563	50-995	50-05 50-76
Hydrogen . .	6-903	7-152	7-148	7-075	6-64 6-64
Nitrogen . .	18-790	18-230	18-470	18-723	18-39 18-31
Oxygen . . .	23-570	23-754	24-819	23-207	24-92 24-29

In concentrated *acetic acid* connective tissue swells up and becomes transparent, but does not dissolve till water is added and heat applied. The acetic solution is not precipitated either by red or by yellow prussiate. In dilute acetic acid, the fibres of connective tissue likewise swell up, becoming transparent and invisible, but do not dissolve, even after several hours' boiling; for on washing with pure water, or neutralising the acid with ammonia, they reappear in their original form. As most of the other textural elements which are intermixed with the connective tissue are not rendered invisible by acetic acid, they are brought more distinctly into view by its application: hence this acid affords valuable aid in the histological study of the tissues. In *alkalis* the fibres also swell up in the gelatinous form, but if the action of the alkali has been continued for some time, they do not reappear on addition of water, but are thereby dissolved.

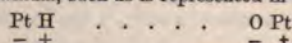
Embryonic connective tissue (Virchow's *mucous tissue*) does not yield gelatin when boiled with water, (Scherer); it consists, in addition to fusiform cells, of a peculiar intercellular substance, which, when digested with water, yields albumin together with a gelatinous or mucous substance. (*Lehmann's Physiological Chemistry*, iii. 46; *Gmelin's Handbuch*, viii. [2] 457).

**CONNELLITE.** A Cornish mineral, consisting of cupric chloride, sulphate, and water, forming small fibrous crystals, belonging to the hexagonal system, translucent, of blue colour and glassy lustre, insoluble in water, easily soluble in hydrochloric and nitric acids. (Connell, J. pr. Chem. xlii. 453.)

**CONTACT ACTION.** *Catalytic action, Catalysis.* These terms are applied to a numerous class of chemical actions, in which the combination of two bodies, or the decomposition of a compound, is brought about by the intervention of a substance which shows no tendency to unite with either of the bodies concerned, and remains unaffected by the changes which take place. Berzelius, who first drew attention to this class of actions, supposed that substances acting in this manner possessed a peculiar power which he called "catalytic force" (from *καταλυνει*, to resolve); he regarded this power as a manifestation of electric force, different, however, from the ordinary action of electricity. Mitscherlich designates substances thus acting "contact substances," and the mode of action, as chemical action or combination by contact.

Examples of these contact actions are found both in inorganic and in organic chemistry; *e. g.* the action of platinum and other metals in inducing the combination of oxygen and hydrogen; the rapid decomposition of peroxide of hydrogen by the presence of platinum, silver, fibrin, &c.; the conversion of starch into dextrin and sugar by boiling with acidulated water; the conversion of cane-sugar into grape-sugar by contact with acids; and the numerous and varied phenomena of fermentation and putrefaction.

The connection between these somewhat obscure phenomena and those of ordinary chemical action, is perhaps to be found in the idea suggested by Berzelius, that they are due to some modification of the electric state of the bodies, or, to speak more generally, to a polarisation of the combining or separating atoms induced by the presence of the apparently inactive body. Take, for example, the action of platinum in inducing the combination of oxygen and hydrogen. We know from the effects of Grove's gas-battery (see *ELECTRICITY*), that when two glass tubes containing oxygen and hydrogen respectively are inverted over water, and platinum plates immersed in them, partly in the gas and partly in the water, the plates being also connected by a wire outside the tubes, the gases gradually disappear, and a voltaic circuit is formed, in which the platinum immersed in the hydrogen corresponds to the positive or zinc plate of the ordinary battery. This effect indicates a polarisation of the molecules of hydrogen, oxygen, and platinum, such as is represented in the following diagram:



Now it is highly probable that a similar polarisation and consequent combination of the oxygen and hydrogen takes place when a clean platinum plate or wire, or finely divided platinum, is introduced into a mixture of those gases, the effect of the metal

being due to the facility with which its contiguous particles place themselves in opposite electrical or polar states. The peculiar efficacy of platinum in bringing about such combinations, appears to be related to its medium position in the electrical or chemical series: we know, indeed, from the purely chemical relations of platinum, that it is almost equally disposed to play the part either of a chlorous or acid, or of a positive or basylous element. The more energetic action of the finely-divided metal is of course due to its larger surface, and to the power which such bodies possess of condensing gases within their pores. The decomposition of peroxide of hydrogen, by contact with platinum and other metals, may be supposed to take place in a similar manner.

The polarised state to which we have attributed the action of platinum in these cases is by no means an isolated condition, but one which pervades the whole range of chemical phenomena. That the whole of the molecules composing a voltaic circuit may be regarded as polarised, was pointed out many years ago by Graham (*Elements of Chemistry*, 1st ed., 1841); and that a similar polarised state comes into play in ordinary cases of chemical action, and may serve to account for many phenomena usually regarded as somewhat obscure,—such as the peculiar energy of bodies in the so-called nascent state,—the decomposition of peroxide of hydrogen by certain metallic oxides, which are themselves at the same time reduced to a lower state of oxidation—the

reaction between hydrochloric acid and hydride of copper ( $\overset{+}{\text{Cu}}\text{H} + \overset{+}{\text{H}}\text{Cl} = \overset{+}{\text{Cu}}\text{Cl} + \overset{+}{\text{H}}\text{H}$ )—the mutual decomposition of hydriodic and iodic acids—and many similar phenomena,—was shown by Brodie in his paper "On the condition of certain elements at the moment of chemical change" (*Phil. Trans.* 1850, p. 759); see also CHEMICAL AFFINITY (i. 858). When, therefore, we refer the action of platinum and other metals to chemical or electrical polarity, we merely point out that these phenomena may be regarded as particular cases of a recognised mode of action. Whether the so-called contact actions which are so frequently observed in organic chemistry, such as the action of ferments, and the conversion of starch into sugar by the action of acids, can be explained in a similar manner, is a question which does not at present admit of a decided answer. (See a paper by Dr. T. L. Phipson: *La Force catalytique ou études sur les Phénomènes de Contact*." Haarlem, 1858.)

It not unfrequently happens that reactions are effected with ease by using a considerable excess of one of the reagents, which can be brought about only with difficulty, or not at all, by using only as much of the reagent in question as actually takes part in the chemical change. These reactions may reasonably be regarded as a special class of contact actions, the excess of the reagent facilitating the action of that portion which takes part in the reaction, in much the same way as in other cases, the "contact-substance" promotes the action of a body chemically different from itself. The most probable explanation that has hitherto been suggested of this action of the mass of a reagent, and of catalytic actions in general, is that the contact-substance assists the reaction, by exerting its affinity in the same direction as the bodies striving to react upon another, but under such conditions that it cannot itself undergo alteration. This supposed mode of action will be made more easily intelligible by an example: if oxalic acid is heated with nitric acid until it begins to be oxidised, and water is then added to the mixture until the action ceases, the oxidation immediately begins again on the addition of a small quantity of a protosalt of manganese (Mercer). In this instance, the tendency of the manganous salt to become a manganic salt, acts in the same direction as the attraction of the elements of the oxalic acid for the oxygen of the nitric acid, which is thus decomposed under the influence of both substances acting together, under circumstances in which it would not have been decomposed by either alone; a sesquisalt of manganese being, however, incapable of existing in an acid solution containing oxalic acid, the protosalt of manganese remains unchanged, although aiding by its presence to bring about the reaction. This mode of explaining many cases of so-called action of contact, was first suggested by Mercer (*Brit. Assoc. Rep.* 1842, vol. ix. *Notices and Abstracts*, p. 32); it was further developed by Playfair (*Mem. and Proc. Chem. Soc.* (1847) iii. 348), and is applied by Kekulé (*Lehrb. d. Org. Chem.* i. 142, note) to the explanation not only of such phenomena, but, in the way indicated above, to those commonly referred to the action of mass.

**CONVALLAMARETIN.** A substance produced by the action of acids and alkalis on convallamarin. It separates from the liquid in crystalline spangles, cakes together into a resinous mass on boiling, melts when heated alone, and decomposes by dry distillation. (Walz.)

**CONVALLAMARIN.** A bitter substance contained, together with convallarin, in *Convallaria majalis* (Solomon's seal). It is obtained by diluting and filtering the mother-liquor from which the convallarin has separated, then digesting with animal charcoal, precipitating with tannic acid, and separating the tannic acid with oxide of lead.



Convallamarin is a white powder, having a bitter taste, with peculiar sweetish after-taste, easily soluble in water and alcohol, nearly insoluble in ether. By heating the aqueous solution with dilute sulphuric acid, the convallamarin is resolved into sugar, water, and convallamaretin. Nitric acid colours convallamarin yellow; strong sulphuric acid colours it violet, but the colour disappears on dilution. Alkalis decomposes it, with separation of convallamaretin. (Walz.)

**CONVALLARETIN.** See CONVALLARIN.

**CONVALLARIA.** The flowers of *Convallaria majalis* (Solomon's seal) yield, by distillation with water, a small quantity of a volatile, crystalline, strong-smelling camphoroidal substance, and a bitter principle (Herberger). Walz (N. Jahrb. Pharm. 1858, x. 145) has obtained from this plant two compounds, named convallarin and convallamarin.

In the herb and stalks of lily of the valley, *Convallaria multiflora*, Walz finds asparagin, starch, sugar, citric acid, malic acid, and a crystallisable substance which produces a scratching sensation in the throat.

**CONVALLARIN.** A substance contained in *Convallaria majalis*. The plant, collected during or after the flowering time, is dried, pulverised, and exhausted with alcohol of 0·84; the tincture is precipitated with subacetate of lead; the lead removed from the filtrate by sulphuretted hydrogen; and the crystals of convallarin, which separate on evaporation, are purified by washing with ether.

Convallarin is composed, according to Walz, of  $C^{34}H^{30}O^{11}$ ; it crystallises in right rectangular prisms, is sparingly soluble in water, to which it imparts an irritating taste, and the property of frothing when agitated. By prolonged boiling with acids, it is said to yield sugar and convallaretin,  $C^{28}H^{22}O^8$ , a yellowish-white crystalline mass, soluble in ether, and having a slight resinous taste.

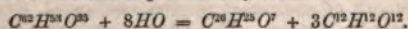
**CONVOLVULIC ACID.** An acid formed from convolvulin, under the influence of bases, by addition of the elements of water. It was first obtained by Kaiser (Ann. Ch. Pharm. li. 30), who called it hydro-rhodeoretin, and assigned to it the formula  $C^{62}H^{50}O^{23}$ , afterwards more fully examined by Mayer (*ibid.* lxxxiii. 126: xcv. 162), who gave it the name rhodeoretic acid, and regarded it as a dibasic acid,  $C^{34}H^{26}O^{10} \cdot H^2$ , or  $C^{72}H^{66}O^{20} \cdot 2HO$ ; subsequently, however, he has considered it as a tribasic acid, with the formula  $C^{36}H^{28}O^{12} \cdot 3HO$  (or sexbasic, according to the formula  $C^{72}H^{56}O^{24} \cdot H^6$ ).

Convolvulic acid is prepared by boiling 100 grammes of convolvulin in 500 grms. of baryta-water with frequent agitation; precipitating the baryta, after cooling, with a slight excess of sulphuric acid; then removing the excess of sulphuric acid by agitation with carbonate of lead; precipitating the dissolved lead by sulphuretted hydrogen, and evaporating the filtrate on the water-bath.

Convolvulic acid is a white, very hygrometric substance, resembling convolvulin in appearance, soluble in all proportions in water and in alcohol, insoluble in ether. The aqueous solution has a strong acid reaction, and a very faint odour like that of quinces. It softens at a few degrees above  $100^\circ C.$ , melts between  $100^\circ$  and  $120^\circ$ , and decomposes at higher temperatures.

It contains, according to the mean of Mayer's analyses, 52·60 per cent. carbon and 7·81 hydrogen, whence Mayer deduces the formula  $C^{88}H^{53}O^{23}$  (52·8 per cent. C, and 7·5 O), representing the acid as convolvulin, plus 3 at. water. This formula is, however, improbable, on account of the uneven numbers of atoms of hydrogen and oxygen.

Convolvulic acid reacts like convolvulin with acetic, nitric, and strong sulphuric acid. By boiling with dilute sulphuric or hydrochloric acid, it is resolved into convolvulinollic acid and glucose; the same effect is produced by emulsin:



Convolvulic acid expels carbonic acid from alkaline and earthy carbonates, especially with the aid of heat. The aqueous solution of the acid, either free or after neutralisation with ammonia, does not precipitate the solution of any neutral metallic salt; but with basic acetate of lead, it yields white bulky flakes.

The acid, boiled with excess of baryta-water, yields a so-called neutral salt,  $C^{62}H^{51}Ba^2O^{23} (?)$ , while if the acid is in excess, an acid salt,  $C^{62}H^{52}BaO^{23} (?)$ , is obtained. Both salts are amorphous, diaphanous, brittle, bitter, with an odour of quinces, very soluble in water and alcohol, melt between  $100^\circ$  and  $110^\circ C.$  A calcium-salt,  $C^{60}H^{51}Ca^2O^{23} (?)$ , obtained by boiling the acid with milk of lime, is amorphous; slightly yellowish: its aqueous solution has a faint odour of quinces.

An acid potassium-salt, containing 5·65 per cent. potash, is obtained by saturating the acid with potash, evaporating to dryness and redissolving in alcohol. It is amorphous, very soluble in water, sparingly in alcohol. The aqueous solution is bitter, and has the odour of quinces. This salt melts between  $100^\circ$  and  $110^\circ C.$  (Mayer.)

**CONVOLVULIN.** A resin contained in the tuberose or officinal jalap-root (the rhizome of *Convolvulus Schiedanus*, Zucc). According to Mayer's last investigations (Ann. Ch. Pharm. xcv. 161), it contains  $C^{21}H^{30}O^{10}$  or  $C^{22}H^{32}O^{10}$ , and is homologous with jalapin, the resin of fusiform jalap (*Convolvulus orizabensis*, Pell). [It may be inferred from Mayer's experiments, though the fact is not distinctly stated, that convolvulin and jalapin exist together in both kinds of jalap-root, the convolvulin being more abundant in the tuberose, the latter in the fusiform species.] Mayer formerly regarded it as  $C^{22}H^{30}O^{10}$  + HO; Kayser (*loc. cit.*) as  $C^{12}H^{13}O^{10}$ ; Laurent as  $C^{16}H^{20}O^{11}$ , or  $C^{22}H^{30}O^{12}$ .

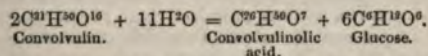
Convolvulin is prepared from the root of *Convolvulus Schiedanus* by exhausting the root with boiling water; drying, and coarsely pulverising it; then treating it three times with twice its weight of alcohol of 90 per cent.; mixing the alcoholic extract with water till it begins to show turbidity; then treating the liquid twice with animal charcoal; distilling the alcohol from the filtrate; repeatedly treating the residual pulverised resin (amounting to between 10 and 15 per cent. of the root) with ether; dissolving the residue in the smallest possible quantity of absolute alcohol; precipitating with ether; and repeating the solution and precipitation till the precipitate is quite free from the portion of the crude resin which is soluble in ether. The residue ultimately obtained is pure convolvulin.

Convolvulin is a colourless transparent resin, which, when pulverised, yields a white powder like gum arabic. It is tasteless and inodorous, nearly insoluble in water, easily soluble in alcohol, but insoluble in ether, whereby it is distinguished from jalapin; the alcoholic solution has a slight acid reaction. The resin melts below  $100^{\circ}$  C. when moist; but in the dry state it softens only at  $141^{\circ}$ , and melts at  $150^{\circ}$  to a light yellow transparent liquid; above  $155^{\circ}$  it begins to decompose. When heated in the air on platinum foil, it burns with a smoky flame, diffusing an odour like that of caramel.

Convolvulin, dried at  $150^{\circ}$  C., contains, according to Mayer's analysis, from 54.21 to 55.01 per cent. carbon, and 7.89 to 8.07 hydrogen; the formula,  $C^{21}H^{30}O^{10}$ , requires 54.97 C and 7.37 H.

Finely divided convolvulin dissolves in aqueous alkalis even in the cold, more easily when heated, and is converted into convolvulic acid. It dissolves also in acetic acid. Very dilute nitric acid dissolves it slowly in the cold, more readily when heated, but with decomposition. Stronger nitric acid decomposes it immediately, with evolution of nitrous acid and formation of oxalic acid and ipomeic acid, an isomer of sebacic acid ( $C^{16}H^{18}O^4$ ).

Convolvulin dissolved in alcohol is resolved by hydrochloric acid into convolvulinolic acid and glucose:



Convolvulin is not affected by cold dilute sulphuric acid; but, when triturated with strong sulphuric acid, it dissolves with fine carmine-red colour, changing after a while to brown; the solution after standing for a longer time deposits a brown-black substance. In this reaction also, convolvulin is resolved into convolvulinol and glucose. It is therefore a glucoside.

Convolvulin is the active principle of jalap-resin; it exerts a very strong purgative action, even in doses of a few grains.

**CONVOLVULINOLIC ACID.** *Convolvulinol, Rhodocortinol.* (Kaiser, *loc. cit.*—Mayer, *loc. cit.*)—This compound is produced, together with glucose, by the action of dilute acids, or of emulsin, on convolvulic acid. To prepare it, 30 grms. of convolvulic acid are dissolved in 300 grms. of water, the solution is heated to the boiling point, and 20 grms. of strong sulphuric acid diluted with 200 grms. of water are added to it, the boiling being continued for some time. Convolvulinolic acid then partly separates as an oil, partly remains dissolved in the water, and separates in colourless microscopic needles on cooling. It is inodorous, but has a harsh, slightly bitter taste. It dissolves but very sparingly in pure water, more freely in acidulated water, very easily in alcohol, less easily in ether; it does not crystallise either from alcohol or from ether. It feels greasy and softens between the fingers, melts at  $38.5^{\circ}$  or  $39^{\circ}$  C. to a yellow oily liquid, and solidifies again at  $36^{\circ}$ . The melted acid, diffused in water, imparts to it a peculiar odour like that of the carob bean.

Heated on platinum foil in contact with the air, it appears to volatilise for the most part without decomposition, the vapours having a strong cough-exciting odour like that of sebacic acid. Strong sulphuric acid colours convolvulinol, first yellowish, then amaranth-red, like convolvulin. Strong nitric acid oxidises it to oxalic and ipomeic acids.

Convolvulinolic acid, prepared as above, contains, according to the mean of Mayer's



analyses, 65.47 per cent. carbon and 10.71 hydrogen, whence he deduces the improbable formula  $C^{26}H^{23}O^7$  (65.8 per cent. C, and 10.5 H). When separated from its salts, however, it has, according to Mayer, the composition  $C^{26}H^{24}O^6$ . A product having this composition is likewise obtained by heating convolvulin or convolvulic acid with hydrate of sodium and a little water, as long as hydrogen continues to escape, decomposing the aqueous solution of the product with sulphuric acid, and purifying by solution in alcohol, and treatment with animal charcoal. It resembles the preceding in all its properties, excepting that it melts at a somewhat higher temperature ( $40^{\circ}$ — $45^{\circ}$  C.), and has a stronger acid reaction.

Mayer applies the term convolvulinol to the product of the action of acids on convolvulic acid, and designates as convolvulinolic acid the compound separated from the convolvulinolates, or obtained by the process last described; but it is most probable that the two substances are merely the same acid in different states of hydration. All these products require re-examination.

The convolvulinolates are composed, according to Mayer, of  $C^{26}H^{24}MO^7$ , or  $MO.C^{26}H^{24}O^6$ . Those of the alkali-metals are easily soluble in water and in alcohol, and are obtained by treating the alcoholic solution of the acid with caustic alkalis. Those of the alkaline-earth metals are sparingly soluble, and are obtained in like manner. Those of most of the heavy metals are insoluble and are obtained by precipitation. The lead-salt is said to contain  $C^{26}H^{22}PbO^6$ . (Mayer.)

**CONVOLVULACEÆ.** An order of plants yielding many useful products. The roots of several species of *Convolvulus* and *Ipomœa* yield purgative resins, or gum-resins. *Convolvulus scammonium*, L., yields scammony (q. v.). *C. Schiedanus* and *C. orizabensis*, or *Ipomœa orizabensis*, yield jalap. *C. turpethum*, or *I. turpethum*, also yields a purgative resin. *C. batatas*, or *Batatas edulis*, the Spanish potato, yields edible tubers, resembling the common potato, but of sweeter taste (i. 520). *C. scoparius*, L., and *C. floridus*, L., yield one of the woods called rose-wood.

**CONYDRINE.** See CONHYDRINE (p. 1).

**COPAHENE or COPAIVENE.** } See COPAIBA OIL.  
**COPAHILENE.** }

**COPAHUVIC or COPAIVIC ACID.** See COPAIBA RESINS.

**COPAIBA BALSAM.** See BALSAMS (i. 492).

**COPAIBA OIL.** *Essence de Copahu.* (Bonastre [1825], J. Pharm. xi. 529.—Ader, J. Pharm. xv. 95.—Gerber, Br. Arch. xxx. 157.—Blanchet, Ann. Ch. Pharm. vii. 156.—Soubeiran and Capitaine, J. Pharm. xxvi. 70.—Gm. xiv. 286.)—The volatile oil contained in balsam of copaiba. It belongs to the camphenes,  $C^{10}H^{16}$ , or  $C^{20}H^{24}$ . Copaiba balsam is a mixture of this oil with resins, the proportion of the oil varying from 30 to 50 per cent. in balsams from different localities.

The oil is obtained by distilling the balsam with water, and may be purified by drying over chloride of calcium and rectifying. To obtain the whole of the oil, the distillation with water must be repeated six or eight times (Soubeiran and Capitaine). According to Ader, the oil may be separated by agitating 100 pts. of the balsam with an equal quantity of alcohol of specific gravity 0.836, then adding  $37\frac{1}{2}$  pts. of soda-ley of specific gravity 1.33, and diluting the whole with 150 pts. of water. The oil then gradually rises to the surface.

Pure oil of copaiba is transparent, colourless, or yellowish-green, mobile, and has an aromatic odour like that of the balsam; that obtained by Ader's method is said to have a more disagreeable odour; the taste is sharp and persistently bitter. Specific gravity 0.881—0.91, increasing to 0.96 on exposure to the air. Boiling-point  $245^{\circ}$ — $260^{\circ}$  C. Optical rotatory power =  $34.18^{\circ}$  to the left. Expansion from  $0^{\circ}$  to  $100^{\circ}$  C. = 0.083132; from  $100^{\circ}$  to  $200^{\circ}$  = 0.104034 (Aubergier, J. Pharm. xvii. 278). The oil is neutral. It solidifies, partly crystalline, at  $-26^{\circ}$  C. Oil of copaiba dissolves in  $2\frac{1}{2}$  pts. of absolute alcohol, and in 25—30 pts. of alcohol of specific gravity 0.85. (According to Stoltze, it dissolves in all proportions in alcohol of this strength.) With sulphide of carbon and anhydrous ether, it mixes in all proportions, but not with more than half its weight of common ether. It dissolves sulphur and phosphorus with aid of heat. It likewise dissolves glacial acetic acid and hydrocyanic acid, and mixes with alcoholic succinic and benzoic acids; also with solution of oxalic acid, but not with citric acid. It absorbs ammonia, becoming milk-white and viscid. (Gerber.)

Copaiba oil becomes brown and viscid by continued boiling. Chlorine in sunshine makes it hot, colours it yellowish blue, and then green, and separates white crystalline masses (Blanchet). Iodine, slowly added to the oil, dissolves without detonation (Blanchet), forming a reddish-yellow, or brown-black liquid: if it be added more quickly, heating and frothing take place, and a brown mass is formed (Gerber). It detonates with fuming nitric acid, leaving a brown resin. With nitric acid of specific gravity



1.32, it resinises only when heated (Blanchet). According to Bonastre, it assumes a violet tint at the beginning of the action. Weaker nitric acid forms with the oil a small quantity of yellow resin, precipitable by water (Gerber). Oil of vitriol makes it hot and turns it red-brown (Stoltze). With a few drops of oil of vitriol it becomes hot and blacker; but when dropped into a larger quantity of oil of vitriol, it forms a red-brown solution of sulphoterebic acid. (Gerhardt, *Compt. rend.* xvii. 314.)

With *hydrochloric acid*, copaiba oil forms a solid and a liquid compound. The oil, shaken up with *aqueous potash* or *soda*, becomes heated, acquires a brown colour, and yields to water a small quantity of resin, which does not pre-exist in the oil, but is produced from it by the action of the alkali (Gerber). Distilled with 24 pts. water and 8 pts. chloride of lime, it gives off carbonic acid and forms chloroform. Distilled with *hypobromite of potassium*, it forms bromoform. (Chautard, *Compt. rend.* xxxiv. 485.)

*a. Hydrochlorate of Copahene or Copaivene. Hydrochlorate of Copaiba oil. Camphre de Copahu.*  $C^{10}H^{16}.2HCl$ .—This is the solid hydrochlorate; it is prepared by passing dry hydrochloric acid gas through dehydrated oil of copaiba, separating the crystalline mass, which is deposited therefrom on cooling, from the brown oil, pressing it between filtering paper, mixing its solution in ether with alcohol of specific gravity 0.85, and washing with alcohol the crystalline mass which separates. (Blanchet.)

Hydrochlorate of copahene forms short, transparent, right rectangular prisms (resembling chlorate of potassium, according to Blanchet), which melt at  $77^{\circ}C$ . (Soubeiran and Capitaine). They are inodorous (Blanchet, Soubeiran and Capitaine); have a faint camphorous odour, and an aromatic bitter taste. (Gerber.)

The hydrochlorate, heated to  $140^{\circ}$ – $150^{\circ}C$ ., gives off a large quantity of hydrochloric acid gas (Soubeiran and Capitaine). When set on fire, it burns with a bright flame (Gerber). Nitric acid, heated with it, is said to give off nitrogen gas (Blanchet). Oil of vitriol, with aid of heat, dissolves it, and deposits it again in the crystalline form on cooling; at a stronger heat, the solution gives off hydrochloric acid gas. Heated with *sulphide of lead*, it yields an oil having an alliaceous odour. Its alcoholic solution is precipitated by *nitrate of silver* or *mercurous nitrate*. (Blanchet.)

It is insoluble in water and in cold alcohol, sparingly soluble in hot alcohol, easily soluble in ether (Blanchet). The alcoholic solution leaves when evaporated a thick oil, which smells like balsam of copaiba, and appears to hold in solution undecomposed dihydrochlorate of copaiba oil. (Soubeiran and Capitaine.)

*Hydrochlorate of Copahilene.*—This is the liquid portion of the product obtained by treating copaiba oil with hydrochloric acid. It always contains in solution a portion of the solid compound, which cannot be separated from it (Soubeiran and Capitaine). It is a black, viscid oil, smelling like castoreum, and without action on polarised light (Soubeiran and Capitaine). When distilled, it gives off hydrochloric acid gas, and yields a colourless oil, which is a solution of hydrochlorate of copahene (Soubeiran and Capitaine). It burns with a faint odour of hydrochloric acid. It gives up a portion of its hydrochloric acid when shaken up with water. It is soluble in alcohol and ether. (Gerber.)

*Para-copaiba Oil.* (Soubeiran and Capitaine [1840]. *J. Pharm.* xxvi. 70.—Posselt, *Ann. Pharm.* lxi. 67.)—This oil occurs in a variety of copaiba balsam from Brazil. It is separated by distilling with water, and the oil is dehydrated with chloride of calcium (Posselt). It is a transparent, colourless, viscid oil, of specific gravity 0.91 (0.898 according to Soubeiran and Capitaine), boiling at  $250^{\circ}C$ . It smells like the balsam, and has a sharp burning taste (Posselt). Rotatory power  $28.553^{\circ}$  to the left (Soubeiran and Capitaine). It dissolves in all proportions in ether, less easily in absolute alcohol, still less in common alcohol.

The oil becomes yellowish when boiled, afterwards brown, thick, tenacious, and charred (Posselt). Chlorine converts it, with evolution of hydrochloric acid, into a yellow sticky mass. The oil dissolves iodine without detonation. With *fuming nitric acid*, it detonates even in the cold; but nitric acid of specific gravity 1.32 resinises it only with aid of heat. Dilute nitric acid, heated with the oil, dissolves it completely after a few days, giving off pitrous acid, carbonic acid, and other volatile acids. From the solution of the oil in nitric acid, water throws down, after evaporation, a reddish-yellow acid resin, sparingly soluble in hot water, easily soluble in alcohol and ether, whilst a peculiar acid remains dissolved, which, when the solution is concentrated by evaporation, crystallises in slender, colourless, transparent laminae, easily soluble in water, alcohol, ether, and rock-oil, inodorous, having a bitter taste, and a slight acid reaction (Posselt). The oil absorbs *hydrochloric acid gas* with avidity, turning brown-red and fuming in the air, but not depositing any crystals on cooling.



**COPAIBA-RESINS.** (Schweizer, Pogg. Ann. xvii. 784; xxi. 172.—Rose, *ibid.* xxxiii. 83.—Hess, Ann. Ch. Pharm. xxix. 140.—Fehling, *ibid.* xl. 110.—Posselt, *ibid.* lxix. 67.)—Copaiba balsam contains several resins which remain behind after the distillation of the volatile oil; certain samples of this balsam have been found to contain peculiar resins.

The resins obtained from ordinary copaiba balsam may be separated into a crystallisable resin called copaivic acid (the  $\alpha$ -resin of Berzelius), and an uncrystallisable  $\beta$ -resin. The latter, which forms but a small proportion of the whole, remains behind, when the entire mass of resin is treated with cold rock-oil, as a brown unctuous mass, easily soluble in alcohol or ether.

**COPAIVIC ACID.** *Copahuic acid.  $\alpha$ -resin of Berzelius.*  $C^{20}H^{30}O^2$ , or  $C^{10}H^{15}O^1$ .—This crystallisable resin exists in copaiba balsam to an amount varying from 20 to 66 per cent. It is the constituent which determines the hardening of the balsam by magnesia, an effect which, however, does not take place if the proportion of copaivic acid is below 50 per cent. (Procter). According to Schweizer, the acid may be prepared by dissolving the entire mass of resins obtained from copaiba balsam in aqueous ammonia, and leaving the solution to evaporate in a cool place. Crystals then separate which may be obtained pure by washing with ether and recrystallisation from alcohol. Or the resinous mass is heated with cold rock-oil, the solution left to evaporate, the residue dissolved in alcohol, and the copaivic acid left to crystallise by spontaneous evaporation. Or the entire mass is dissolved in alcohol, and the solution left to evaporate.

Copaivic acid forms colourless rhombic crystals, soluble in strong alcohol; the solution reddens litmus. It dissolves easily in ether, in oils both fixed and volatile, and in sulphide of carbon. It is decomposed by heating.

The acid dissolves in aqueous fixed alkalis and in ammonia. The alcoholic solution mixes without decomposition with alcoholic potash or with strong aqueous potash; but, on adding a larger quantity of water, a precipitate is formed.

Copaivic acid appears to be monobasic. The *calcium-salt*,  $C^{20}H^{30}CaO^2$ , is a white precipitate, which separates on mixing an alcoholic solution of the resin containing a little ammonia with alcoholic chloride of calcium, and then adding water. *Copaivate of lead*,  $C^{20}H^{30}PbO^2$ , is obtained by mixing the alcoholic solutions of the resin and acetate of lead, as a white, fusible, slightly crystalline precipitate. *Copaivate of silver*,  $C^{20}H^{30}AgO^2$ , separates, on mixing the solution of the resin with an alcoholic solution of nitrate of silver mixed with a little ammonia, as a white crystalline precipitate, sparingly soluble in alcohol, easily soluble in ammonia, easily fusible, and turning brown on exposure to light.

**OXYCOPAIVIC ACID.**  $C^{30}H^{40}O^3$ , or  $HO.C^{15}H^{20}O^2$ .—This acid resin was found by Fehling in a sediment deposited from a turbid copaiba balsam from Para. By solution in alcohol and slow evaporation, it is obtained in colourless regular crystals, whose primary form is a rhombic prism having the acute summits truncated. It becomes strongly electric by friction; dissolves readily in ether, less readily in alcohol; melts at about  $120^\circ C$ . When the solution of the resin in ether and alcohol is quickly evaporated in a flat dish, and stirred at the same time, a hydrated resin,  $C^{30}H^{40}O^3.H^2O$ , or  $C^{30}H^{38}O^3.2HO$ , sometimes separates as an amorphous powder; it has the same composition as the oxysilvic acid described by Hess, but differs from it in properties. This hydrated resin softens in boiling water; it forms with bases the same salts as the anhydrous resin.

Oxycopaivic acid, heated with *nitric acid*, gives off carbonic and nitrous acids, and yields two products, a resin and a new acid. The resin, said to be  $C^{30}H^{40}O^{15}$ , is light yellow, has a strong and disagreeably bitter taste, and unites with bases. The acid is free from nitrogen, of brownish colour, deliquescent, very soluble in water and in alcohol, easily decomposes carbonates, forms soluble salts with the alkalis, a sparingly soluble salt with baryta, insoluble salts with lead, mercury, and silver; the lead-salt has the composition  $2PbO.C^{15}H^{20}O^2$ , or  $4PbO.C^{30}H^{40}O^4$  (?).

When oxycopaivic acid is evaporated to dryness with nitric acid, there remains a pitchy mass, part of which dissolves in alcohol, leaving a humoidal substance having the composition  $C^8H^8O^2$ .

**Oxycopaivates.**—Oxycopaivic acid dissolved in alcohol exhibits an acid reaction. The oxycopaivates of the *alkali-metals* are soluble in water; the ammoniacal solution gives off all its ammonia by evaporation. The *lead-salt*,  $C^{30}H^{40}PbO^3$ , or  $PbO.C^{15}H^{20}O^2$ , is obtained as a white precipitate on mixing the alcoholic solution of the resin containing a little ammonia with an alcoholic solution of acetate of lead. The *silversalt*,  $C^{30}H^{40}AgO^3$ , or  $AgO.C^{15}H^{20}O^2$ , separates as a white amorphous precipitate on mixing a solution of the acid in aqueous ammonia with excess of nitrate of silver.

**ACID COPAIBA-RESIN.**—This resin was found by Martin and Vigne (J. Pharm.

1842, p. 52), in a crystalline deposit of copaiba balsam, which dissolved in hot alcohol, but separated out again for the most part as the solution cooled. As it has not been further investigated, its identity or non-identity with one of the resins previously described, must for the present remain undecided.

From clear copaiba balsam, Martin and Vigne prepared a resin different from the crystalline substance.

**INDIFFERENT COPAIBA-RESINS.**—Whether the  $\beta$ -resin (p. 18) belongs to this group is doubtful, inasmuch as it is said to dissolve in alkalis.

In a very fluid copaiba balsam of peculiar constitution, Posselt found, besides para-copaiba oil, two indifferent amorphous resins, the first of which (containing 60·3 per cent. carbon, 8·3 hydrogen, and 31·4 oxygen) was soluble in weak boiling alcohol; the second (containing 82·0 carbon, 10·5 hydrogen, and 7·5 oxygen) dissolved sparingly in boiling absolute alcohol, separated out for the most part on cooling, and was insoluble in dilute alcohol. Neither of these resins combines with alkalis. (Handw. d. Chem. ii. [8] 799.)

**COPAIVENE.** The camphene contained in the crystallised hydrochlorate of copaiba oil; it has not yet been isolated (p. 16).

**COPAIVIC ACID.** See COPAIBA RESINS.

**COPAIVILENE or COPAIVYL.** Syn. with COPAIVENE.

**COPAL.** A valuable resin of which the best coach-varnish is made. It exudes spontaneously from several trees, namely, the *Rhus copallina*, a terebinthaceous tree, native of North America, the *Elaeocarpus copalifer*, which grows in the East Indies, and the *Hymenaea verrucosa*, which grows chiefly in Madagascar. French writers likewise give the name copal to the resin of the *Hymenaea Courbaril*, growing in Brazil and the West Indies; but in England and Germany this resin is called *animé* (see vol. i. p. 296). There is altogether a considerable amount of discrepancy in the statements respecting the trees which furnish copal.

Copal generally occurs in flat pieces, rough on the outside, and of various shapes and sizes. Its physical properties vary to a certain extent according to its origin; but the lumps are, for the most part, opaque on the outside, transparent internally, of yellowish to yellowish-brown colour, sometimes nearly colourless; turbid and translucent lumps also occur; insects and parts of plants are not unfrequently enclosed within the resin. Copal is hard; it has a very lustrous conchoidal fracture, is easily pulverised, does not cake together even when chewed, but becomes rather soft at 50° C. The specific gravity of copal varies from 1·045 to 1·139 according to its origin, and perhaps also according to its age.

The solubility of copal in different liquids varies also with its origin, American copal being much less soluble in alcohol, oil of turpentine, and oil of rosemary, than East Indian or African copal. By exposure to the air, especially when pulverised and placed in a hot air-chamber, it absorbs oxygen, and then becomes more soluble in alcohol and in oil of turpentine. The solubility is also increased by melting the copal at the lowest possible temperature; but American copal is more difficult to fuse than the other varieties, and sometimes remains so insoluble as to be quite useless for making varnishes. Anhydrous copal in the natural state is but very sparingly soluble, but swells up to a tough elastic substance when boiled. In pure ether, copal swells up to a transparent jelly, and afterwards changes to a syrupy mass. If this mass be heated to commencing ebullition, and alcohol of specific gravity 0·82 be added in successive small quantities, a clear solution is obtained; but if the alcohol be added cold or all at once, the mass coagulates and does not dissolve. Copal is but partially soluble in sulphide of carbon, but oil of caoutchouc dissolves it easily, even in the cold.

Copal dissolves in strong sulphuric and nitric acids, but is decomposed by those acids if only slightly heated.

The statements respecting the solubility of copal in caustic alkalis vary considerably, doubtless because the experiments have been made upon different varieties. According to Filhol, neither ammonia nor potash dissolves it in the cold; but if the liquid is heated to the boiling point, the resin coagulates and floats on the surface in the form of a spongy mass, which does not dissolve, even after several hours' boiling,—because the compound of the resin with the alkali, though soluble in pure water, is quite insoluble in water containing excess of alkali.

The following analyses of various kinds of copal have been made by Filhol:

	Copal from Calcutta, in tears.	Copal from Calcutta, in very white, flat lumps.		Copal from Bombay.	Copal from Madagascar.
Carbon . . .	80·66	80·34	80·29	79·70	79·80
Hydrogen . . .	8·77	10·32	10·52	10·40	9·42
Oxygen . . .	10·57	9·14	9·14	9·90	10·78
	100·00	100·00	100·00	100·00	100·00
		c 2			



Filhol has obtained from East Indian copal, five distinct resins, some of which however pass into others by oxidation, so that they may be regarded as different oxides of the same radicle; viz.:

*a-resin*: Soft, fusible at the heat of the water bath; soluble in alcohol of 72 per cent., also in ether, and in oil of turpentine; forms, with bases, resinsates soluble in ether, but (excepting the potassium-salt) insoluble in alcohol.

*β-resin*: Soft, fusible below 100° C.; soluble in all proportions in alcohol, ether and oil of turpentine; forms resinsates soluble in ether, insoluble in absolute alcohol.

*γ-resin*: White, soluble in absolute alcohol and in ether; less fusible than the preceding; forms resinsates insoluble in alcohol and ether.

*δ-resin*: White, insoluble in alcohol and ether, soluble in alcoholic potash; very difficult to fuse.

*ε-resin*: Gelatinous; insoluble in all menstrua.

These resins yielded by analysis:

	Carbon.	Hydrogen.
<i>a-resin</i> . . .	77.76 to 76.94	10.12 to 10.24
<i>β-resin</i> . . .	76.04 — 76.85	10.03 — 10.86
<i>γ-resin</i> . . .	80.53 — 80.70	10.43 — 10.66
<i>ε-resin</i> . . .	81.16 — 81.68	10.54 — 10.43

The lead-salts formed from the first two yielded:

	<sup>α</sup>	<sup>β</sup>
Oxide of lead . . .	26.17 to 26.32	25 to 28

These analyses were perhaps not made with definite substances. The quantities of lead-oxide found in the resinsates are nearly the same as in the lead-salts obtained from the turpentine-resins (see TURPENTINE); hence it is probable that the resinous constituents of copal are similar in composition to the resins of turpentine. (Gerh. iii. 669; Handw. d. Chem. ii. [3] 202.)

**COPAL VARNISH.** Copal may be dissolved by digestion in linseed oil, rendered drying by quicklime, with a heat very little less than sufficient to boil or decompose the oil. This solution, diluted with oil of turpentine, forms a beautiful transparent varnish, which, when properly applied, and slowly dried, is very hard and durable. This varnish is applied to snuff-boxes, tea-boards, and other utensils. It preserves and gives lustre to paintings, and greatly restores the decayed colours of old pictures, by filling up the cracks, and rendering the surfaces capable of reflecting light more uniformly.

Mr. Sheldrake has found, that camphor has a powerful action on copal; for if powdered copal be triturated with a little camphor, it softens, and becomes a coherent mass; and camphor, added either to alcohol or oil of turpentine, renders it a solvent of copal. Half an ounce of camphor is sufficient for a quart of oil of turpentine, which should be of the best quality; and the copal, about the quantity of a large walnut, should be broken into very small pieces, but not reduced to a fine powder. The mixture should be set on a fire so brisk as to make the mixture boil almost immediately; and the vessel should be of tin or other metal, strong, shaped like a wine-bottle with a long neck, and capable of holding two quarts. The mouth is stopped with a cork, in which a notch is cut to prevent the vessel from bursting. It is probably owing to the quantity of camphor it contains, that oil of lavender is a solvent of copal. Camphor and alcohol dissolve copal still more readily than camphor and oil of turpentine.

In the 51st volume of Tilloch's Magazine, Mr. Cornelius Varley states, that a good varnish may be made by pouring upon the purest lumps of copal, reduced to a fine mass in a mortar, colourless spirits of turpentine, to about one-third higher than the copal, and triturating the mixture occasionally in the course of the day. Next morning it may be poured off into a bottle for use. Successive portions of oil of turpentine may thus be worked with the same copal mass. Camphorated oil of turpentine, and oil of spike-lavender, are also recommended as separate solvents, without trituration. The latter, however, though very good for drawings or prints, will not do for varnishing pictures, as it dissolves the paint underneath, and runs down while drying.

*Fat varnish.*—Take copal 16 parts, linseed or poppy oil made drying with litharge 8, oil of turpentine 16. Melt the copal in a matrass, by exposing it to a moderate heat; pour then upon it the boiling-hot oil; stir the mixture, and when the temperature has fallen to about 200° F. add the oil of turpentine heated. Strain the whole immediately through linen cloth, and keep the varnish in a wide-mouthed bottle. It becomes very clear in a little while, and is almost colourless when well made. This varnish is applied on coaches, also generally on polished iron, brass, copper, and wood.—U.

**COPALIN.** *Fossil copal, Highgate resin.*—A fossil resin found in roundish lumps in the blue clay of Highgate Hill. It resembles copal resin in hardness, colour, lustre, and transparency, and is likewise but sparingly soluble in alcohol. Sp. gr. 1.010 (Johnston), 1.05 (Bastick). It emits a resinous odour when broken, volatilises in the air at a gentle heat, and burns easily with yellow flame and much smoke. Sulphuric acid dissolves it with purple-brown colour. Nitric acid converts it into an acid resin, which is precipitated by water as a yellow powder, forms soluble salts with the alkali-metals, insoluble with all the rest. According to Johnston's analysis (Phil. Mag. [3] xiv. 87), it contains 85.4 per cent. carbon, and 11.8 hydrogen, 2.7 oxygen, and 0.13 ash, whence may be deduced the formula  $C^{85}H^{11.8}O$  or  $C^{85}H^{11.8}O_2$ . (Johnston, from the old atomic weight of carbon,  $C = 6.12$ , calculated the formula  $C^{85}H^{11.8}O$ .)

Kenngott obtained from India a resin which agreed with the Highgate resin in properties, and had a specific gravity of 1.053; it contained fragments of Alpine plants and insects. An analysis by Duflos showed it to contain 85.73 per cent. carbon, 11.50 hydrogen, and 2.77 oxygen.

Another resin, resembling the preceding in external appearance, occurs in the form of flattened drops or coatings on calcespar, on the walls of a dyke of trap at the old lead mine in Northumberland called *Settling Stones*. It has a pale yellow to deep red colour, with pale green opalescence. Sp. gr. 1.16—1.54; hard, but brittle; does not melt at 400° F., but burns in the flame of a candle with empyreumatic odour. It is insoluble in water, and nearly insoluble in alcohol. It contains 85.13 per cent. carbon, 10.85 hydrogen, and 3.26 ash = 99.24, numbers agreeing nearly with the formula  $C^8H^8$ . (Dana, ii. 267.)

**COPIAPITE.** *Yellow Copperas.*—A hydrated basic ferric sulphate,  $2Fe^2O^3.5SO^4 + 3HO$ , occurring in the district of Copiapo in the province of Coquimbo, in northern Chili, in six-sided tables and grains, which cleave readily parallel to the base. Also fibrous and incrusting. It is translucent, with yellow colour and vitreous lustre. Several other basic ferric sulphates are also found native, viz. *Stypticite* and *Fibroferrite* from Chili, *Pitticite* from Fahlun in Sweden, and *Misy* found near Gesler in the Harz; they are formed by the weathering of iron pyrites, and are probably not definite compounds. (See SULPHATES.)

**COPPER.** Synonyms: *Kupfer, Cuivre, Cuprum, Venus*. Symbols and Atomic weights: Cu = 31.6 (*cupricum*); Ccu = 73.2 (*cuprosum*.)

Copper has been known from the earliest times, and appears to have been used for weapons, tools, and agricultural implements much earlier than iron. It was indeed much more likely to attract the attention of primitive nations than iron, as it is found naturally in the metallic state, is malleable and ductile immediately after fusion, and acquires considerable hardness when mixed with other metals. Isidorus, who wrote at the beginning of the seventh century, says: "Apud antiquos priore æris quam ferri cognitum usum, ære quippe primi proscindebant terram, ære certamina belli gerebant." The Romans, who obtained it from the island of Cyprus, called it *æs cyprum*, a term afterwards shortened into *cyprum*, which ultimately became *cuprum*. The Greeks called it χαλκός, from Chalcis in Eubœa, another locality whence it was obtained. Both the Greek χαλκός and the Roman *æs* appear, however, to have been used indifferently for copper, bronze, and brass. Pliny uses the word *æs* in both senses, as appears from the following passages: "*Æs fit a lapide æroso quem vocant cadmiam*," which probably refers to brass; and again, "*Fit et ex alio lapide quem chalcitem vocant in Cypro, ubi prima fuit æris inventio*," where *æs* appears to signify copper.

*Occurrence.*—Copper occurs very abundantly and in a great variety of forms. It is found in the metallic state; also as oxide, chloride, carbonate, phosphate, sulphate, silicate, arsenate, and vanadate; as sulphide, sometimes alone, but more frequently in combination with the sulphides of other metals, as in copper-pyrites, purple copper, and the several varieties of fahl-ore. It is found to the amount of 0.1 to 0.2 per cent. in many specimens of meteoric iron. According to Walechner (Compt. rend. xxiii. 12), copper is as widely distributed in nature as iron, though less abundantly, small quantities of it being invariably found in iron-ores, in soils, and in ferruginous mineral waters. It has also been found in sea-weed (Malaguti, Durocher, and Sarzeau, Ann. Ch. Phys. [3] xxviii. 129), a fact which proves its existence in sea-water,—in the blood of various *Ascidia* and *Cephalopoda* (Harless, Chem. Gaz. 1848, p. 214), in the blue blood of *Limulus Cyclops* (Genth, Pogg. Ann. xcv. 60), and in very minute quantity in the bodies of animals of higher organisation (Jahresb. d. Chem. 1847-8, pp. 871, 874; 1849, p. 530). According to Odling and Dupré (Guy's Hospital Reports, Oct. 1858), small quantities of copper are constantly found in flour, straw, hay, meat, eggs, cheese, and other articles of food; in the animal organism, it exists in



proportionally large quantity in the liver and the kidneys, while the blood contains only traces of it.

Of the various copper minerals above enumerated, a few only can be regarded as ores of copper, that is to say, as minerals from which the metal can be profitably extracted.

1. *Native copper*.—Metallic copper is not unfrequently found in copper ores, occurring in isolated particles, thin laminae, dendritic pieces, and sometimes in solid blocks. Pieces of ore are sometimes found consisting of a nucleus of metallic copper coated successively with red oxide and with carbonate of copper. Large masses of native copper have been found on the coast of Lake Superior near Keweenaw Point, in veins that intersect the trap and sandstone. Dr. Percy states, on the authority of Professor Brush of Yale College (U. S.), that in 1858, 6000 tons of copper were procured from these deposits; one mass found at Minnesota, weighed 500 tons. Another mass thrown down in 1853 at the North American mine, was 40 feet long, and weighed 200 tons. Native copper is found also in Siberia; in the island of Nalaoe, one of the Faroe group; in many of the Cornish mines; near Harlech, North Wales; and in Brazil, Chili, and Peru. The North American native copper contains about  $\frac{3}{10}$  per cent. of silver, for the most part intimately mixed with it, but sometimes in visible grains, lumps, or threads. The Chili copper also contains silver, sometimes to the amount of 7 or 8 per cent.

2. *Oxides*.—The red oxide,  $\text{Cu}_2\text{O}$ , or  $\text{Cu}^2\text{O}$ , is found in Cornish, South American, and especially in Australian ores. A large vein of it was worked at Chessy in France, but it is now nearly exhausted. When pure it contains 88.78 per cent. of copper.

The black oxide,  $\text{CuO}$ , or  $\text{CuO}$ , occurs at Keweenaw Point, Lake Superior, forming a vein in conglomerate, from which about 40,000 lbs. of ore have been extracted; but it is now exhausted. The pure oxide contains 79.82 per cent. copper.

3. *Carbonates*.—The green carbonate or malachite,  $\text{Cu}^2\text{CO}_3 + \text{H}_2\text{O}$ , or  $\text{CuO.CO}_2 + \text{CuO.HO}$ , occurs abundantly in many localities, especially in Siberia and in South Australia: the pure mineral contains 57.33 per cent. of copper. The blue carbonate or azurite,  $\text{Cu}^2\text{HCO}_4$ , or  $2(\text{CuO.CO}_2) + \text{CuO.HO}$ , is found in considerable quantity at Chessy, near Lyons, and has been imported from South Australia in admixture with the green carbonate. When pure it contains 55.16 per cent. of copper.

4. *Sulphides*.—Vitreous or grey Sulphide of Copper,  $\text{Cu}_2\text{S}$ , or  $\text{Cu}^2\text{S}$ , occurs frequently in Cornwall. It contains 79.79 per cent. copper, but is generally associated with iron to the amount of 0.5 to 3.33 per cent.

*Purple copper*.—This term is applied to several minerals consisting of cuprous and ferric sulphides, combined or mixed in various proportions. Rammelsberg divides them into three classes, the first comprising ores containing 56 to 58 per cent. of copper, the second 60 to 64 per cent., and the third 70 per cent. They form valuable ores, and are abundant in Cornwall, Sweden, and many parts of North America. The mineral  $3\text{Cu}^2\text{S.Fe}^4\text{S}^3$ , or  $3\text{Cu}^2\text{S.Fe}^2\text{S}^3$ , occurs disseminated in the cupriferous shale of the Mansfeld district of Prussian Saxony, and in Pennsylvania.

*Copper pyrites* or *Yellow copper ore*,  $\text{CuFeS}_2$ , or  $\text{Cu}^2\text{S.Fe}^2\text{S}^2$ .—Copper 34.8 per cent. This is the most abundant ore of copper, and is found in large quantities in Cornwall and Devonshire, at Fahlun and Ätvidaberg in Sweden, in Cuba, South America, and many parts of the United States. The Cornish mines yield annually from 150,000 to 160,000 tons of this ore, from which 10,000 to 12,000 tons of pure copper are smelted: the Cornish ore is imbedded in quartz; that of Sweden in gneiss.

*Fahl-ore*, or *True Grey copper ore*.—This term includes a considerable number of minerals consisting of protosulphide of copper combined with the sulphides of antimony and arsenic, the copper being more or less replaced by iron, zinc, silver, and mercury. The copper varies from 30 to 48 per cent., according to the foreign metals present; the mercury varies from 2 to 15 per cent. Fahl-ores not containing silver are the richest in copper, containing 48 per cent.; in the most highly argentiferous ores, on the other hand, some of which contain 31 per cent. silver, the proportion of copper may be as low as 15 per cent.—*Bournonite* is a sulphantimonite of copper and lead, containing 41.7 per cent. Pb, and 12.7 per cent. Cu, sometimes with a small quantity of iron. These ores occur in numerous localities, and often very abundantly.

*Atacamite*, the native oxychloride of copper from Peru and Chili, and *chrysocolla*, the native silicate found associated with other copper ores in various localities, are likewise used for the extraction of the metal.

The sulphuretted ores of copper are found in veins traversing the ancient rocks. Near these primitive veins are often found beds of copper ores, evidently arising from decomposition of the mineral in the vein by the action of water. The first change consists in the conversion of the sulphide of copper into sulphate by the oxidating action of the air contained in the water; the sulphate then dissolves, and is carried away by



the water; and when this cupreous solution filters through beds of carbonate of calcium, or remains in the cavities of such calcareous beds, double decomposition takes place, resulting in the formation of sulphate of calcium, which is carried away by the water, and carbonate of copper, which is deposited. If this reaction takes place at a high temperature, oxide of copper is deposited, instead of carbonate; and, if organic substances are present, the copper may be reduced to sulphide or red oxide, or even to the metallic state. This reaction may explain the occurrence of beds of carbonate and oxide of copper so frequently found in the neighbourhood of veins of copper pyrites, and of the small crystals of sulphide of copper, which are found disseminated through certain bituminous schists, as in the Mansfeld district of Prussian Saxony.

#### *Preparation of Metallic Copper.*

The processes of copper-smelting vary greatly according to the nature of the ore. The treatment of the oxides and carbonates of copper is comparatively simple, the reduction being effected by melting the ore in contact with charcoal, or other carbonaceous matter, and a siliceous flux. The oxide of copper has, however, a strong tendency to unite with the silica, forming a highly cupriferous slag. To prevent the loss thence arising, it is necessary either to add a strong base, with which the silica may unite in preference to the oxide of copper, or else a quantity of copper pyrites, iron pyrites, or other sulphuretted ore, the sulphur in which may combine with the oxygen, and reduce the copper to the metallic state, thereby preventing it from forming a silicate. The first method is adopted at Chessy, where copper ores, consisting of malachite, azurite, and red oxide, mixed with clay, hydrated oxide of iron, and calamine, are smelted with coke and lime. The second method is practised at the copper works in the Ural, where a mixture of copper ores, consisting of native copper imbedded in quartz and magnetic iron ore, malachite, red and black oxide of copper, &c., and copper pyrites, is smelted in blast furnaces fed with wood. The metal obtained by these operations is an impure copper, called *black copper* (*Schwarzkupfer*, *cuivre noir*), which is purified or refined by processes to be hereafter described.

*Sulphuretted copper ores* require a much more complicated treatment, depending mainly on the fact that copper has a greater affinity for sulphur, and a less affinity for oxygen, than iron and the other metals with which it is associated. They are first *roasted*, to convert a considerable portion of the sulphides into oxides; then the roasted ore is melted, either in reverberatory or in blast furnaces, with addition of slag and other fluxes, if the ore does not already contain a sufficient proportion of silicates. During this operation, the oxide of copper formed in the roasting is reconverted into sulphide, while the iron which remained in the roasted ore as sulphide, passes to the state of oxide. A slag is then formed, containing the greater part of the iron in the ore, and a sulphide of iron and copper (*coarse metal*, *Rohstein*, *matte* *cuivreuse*), containing the greater part of the sulphide of copper in the ore, and a much smaller proportion of sulphide of iron. The coarse metal, which may be described as a concentrated copper ore, is now again roasted or calcined, and the roasted product is again fused with the slags of other operations, frequently also with addition of oxidised copper ores, when such are available. This operation yields a second slag, containing a larger proportion of iron, and a second regulus containing a still larger proportion of sulphide of copper than the first: and by repeating these calcining and melting operations, a certain number of times, varying according to the nature of the ore and the construction of the furnaces, a regulus is at length obtained, consisting almost wholly of sulphide of copper. Now when this compound is roasted, with free access of air, the first result is to oxidise both the sulphur and the copper, the sulphur mainly going off as sulphurous acid, so that after a while there remains a mixture of sulphide and oxide of copper, which compounds, at a certain temperature, decompose each other in such a manner as to yield sulphurous acid and metallic copper (e.g.  $2\text{CuS} + \text{Cu}_2\text{O} = \text{SO}_2 + \text{Cu}$ ). The product of the operation is a regulus of metallic copper, varying considerably in purity according to the particular series of operations to which it has been subjected, and known as *coarse copper*, *blister copper*, *Schwarzkupfer*, *cuivre noir*, &c. This impure metal is lastly subjected to the *refining* process, which is more or less complicated, according to the degree of purity of the coarse copper.

The several operations of calcining and melting are performed either in reverberatory furnaces, or in blast furnaces similar to those used in the smelting of iron, only not so large. The choice of one or the other form of furnace, is determined by the circumstances of the locality. Where there is abundance of coal, and of good fire-clay for the construction of the furnace, as in the neighbourhood of Swansea in South Wales, reverberatory furnaces are used; but where these conditions are not fulfilled, as in most of the continental localities where copper is smelted, the preference is given to blast furnaces, partly because they are less quickly corroded by the action of the



melted slag, partly because they ensure a more economical consumption of the fuel, and less loss of copper in the slags.

*Copper-smelting in Reverberatory Furnaces: Welsh Process.*

Copper-smelting has been carried on in the British Isles from very early times. There are records of copper-works in Northumberland, Cumberland, and Yorkshire in the reign of Edward III.; and smelting works were subsequently established in Lancashire, Staffordshire, Gloucestershire, Cornwall, and the neighbourhood of Bristol, in most cases in the neighbourhood of copper mines. At all these old works, blast-furnaces appear to have been used. In the seventeenth century, copper-smelting was extensively carried on at Neath in South Wales; but at present the largest copper-works in Great Britain are at Swansea, a locality eminently adapted for the purpose, not only by the great abundance of coal in its vicinity, but also by its position on the coast, at a short distance from Cornwall and Devonshire, the counties from which the largest quantities of copper ore are obtained, and easily accessible to vessels conveying ore from Spain, South America, Australia, and other parts of the world.

The ores smelted at Swansea may be divided into five classes:

1. Sulphides of copper, mixed with a large proportion of sulphide of iron, and only a very small quantity of oxidised copper-compounds. The gangue is formed of quartz and earthy matters. Proportion of copper from 3 to 15 per cent.
2. Cupriferous pyrites, similar in composition to the preceding, but containing a larger proportion of copper, viz. 15 to 25 per cent.
3. Cupriferous pyrites containing very little iron pyrites, or any other substance hurtful to the quality of the copper, but a larger proportion of oxidised copper-compounds.
4. Ores consisting chiefly of oxidised copper-compounds, mixed with copper pyrites and purple copper. Gangue quartzose. Proportion of copper 25 to 45 per cent.
5. Very rich oxidised copper ores, free from sulphides and injurious substances; they contain from 60 to 80 per cent. of copper, in the metallic state, and as oxide and carbonate. These choice ores come principally from Chili.

The facility with which the reduction is effected, as well as the quality of the metal produced, depends in great measure on the judicious admixture of these several varieties of ore. When a plentiful supply of oxides or carbonates can be obtained to mix with the sulphides at a certain stage, the number of operations from the first calcination to the refining may be reduced to six; but when only sulphurous ores are at hand, eight, or even ten or twelve operations may be required. The following is an outline of the process, as carried on under the most favourable circumstances.

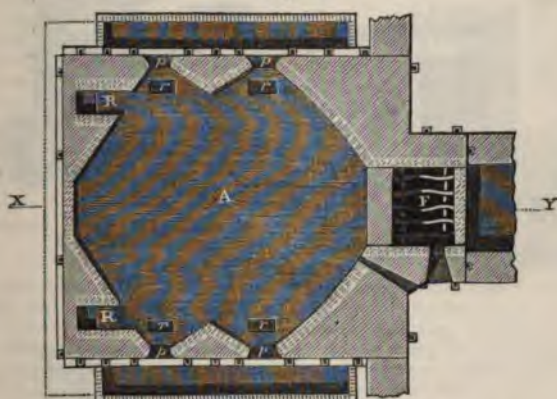
1. *Calcination.*—The process is commenced with ores of the first-class, consisting essentially of the sulphides of copper and iron. They are calcined in a large reverberatory furnace, called the calciner, of which *fig. 132* represents a horizontal section, and *fig. 131* a vertical section through the line X Y of the plan. The hearth of the furnace is formed of fire-brick, and is either square, as represented in the figure, or more frequently oblong, about 20 feet by 12 feet being usual dimensions. The vault descends rapidly from the end above the fire-place F, to the opposite end R, where the gases enter the tall chimney. The furnace is charged with from 3 to 3½ tons of ore, by the cast-iron hoppers T, the charge being uniformly spread over the hearth by means of long iron tools called *stirring rabbles*, introduced by the side doors p, which are four or six in number, according to the length of the furnace. The projections between these doors serve to prevent the charge from getting heaped up in the intervening space, a position from which it could only be removed by stirring from the opposite side. The fuel used is anthracite mixed with ¼ of its weight of bituminous coal, to make it cake together and form a mass of a due degree of porosity. The air passing upwards through this heated mass of carbon, its oxygen is completely converted into carbonic oxide, which, together with the nitrogen, passes on through the body of the furnace, and burns at the expense of the air, which enters by the aperture o (*fig. 132*), situated near the fire-bridge, and by smaller apertures in the side doors; the vault of the furnace thus becomes filled with a long flame of carbonic oxide, burning in contact with the stratum of air containing excess of oxygen, which enters by the apertures above-mentioned, and spreads itself over the hearth. The ore on the hearth is thus constantly immersed in a stratum of oxidising gas, kept at a high temperature by the combustion of the carbonic oxide just above it. A considerable portion of the sulphur in the ore is thus converted into sulphurous acid, which escapes by the chimney, the copper and the iron being at the same time partially converted into oxides. The calcination lasts from 12 to 24 hours, the charge being stirred from time to time to expose a fresh surface to the oxidising atmosphere, and the heat regulated so as not to permit the particles to clot or sinter together, the tendency to which diminishes, how-

ever, as the calcination proceeds. When the calcination is completed, the ore is raked into the holes, *r r*, on the sides of the hearth, through which it falls into the vault *U* below, where water is thrown upon it.

Fig. 131.



Fig. 132.



An idea of the change which takes place in the calcining process, may be gathered from the following analyses of samples of raw and calcined ore, by Le Play. (*Description des procédés métallurgiques employés dans le Pays de Galles pour la fabrication du Cuivre*. Paris, 1848.)

Raw ore.		Calcined ore.	
Cuprous oxide, $\text{Cu}_2\text{O}$	0.4	Sesquisulphide of iron ( $\text{Fe}^3\text{S}_2$ )	5.4
Copper pyrites	22.7		11.2
Iron pyrites, $\text{FeS}$	22.4		11.2
Various sulphides	1.0		0.6
Sesquioxide of iron	0.6		11.7
Various oxides	0.3		0.6
Silica	34.3		34.3
Earthy ashes	2.0		2.0
Water and carbonic acid in combination	0.5	Sulphuric acid combined	1.1
	84.2		78.1
Atmospheric oxygen consumed by this amount of ore in the calcination	15.8	Evolved { Water and carbonic acid 0.5 as gas. { Sulphurous acid. 21.4	21.9
	100.0		100.0

The loss of weight which occurred during calcination, was found to be 7.2 per cent. and the loss of sulphur 51.9 per cent. of the total in the ore.

2. *Melting of the calcined ore.*—This process is performed in a reverberatory furnace, called the ore-furnace, represented in figures 133, 134.

The fuel is a mixture of 2 pts. anthracite and 1 pt. bituminous coal. The temperature

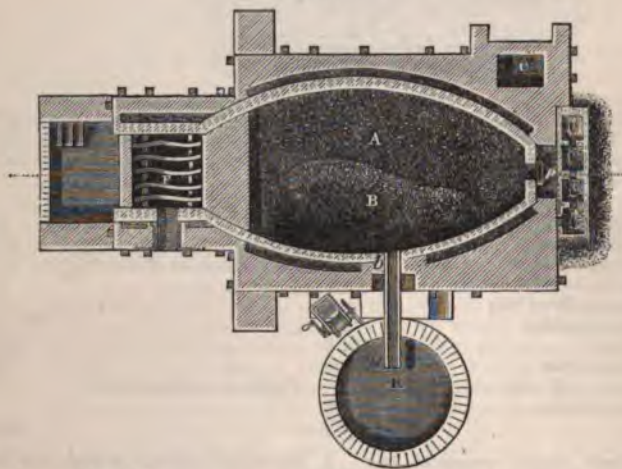


is raised higher than in the calcining furnace, by increasing the draught. The hearth is formed of slag, and has a depressed basin at B, into which the melted metal sinks. The charge consists of the calcined product of the preceding operation mixed with *metal slag*, a product obtained in operation No. 4, and sometimes with unroasted ore of the third class (p. 24), and a certain quantity of fluor spar to render the slag more fluid. The oxides and sulphides decompose one another, the products being chiefly sulphide of copper, oxide of iron, which passes into the slag as silicate, and sulphurous acid, which escapes, the oxidation of the sulphur being also partly due, as in the preceding operation, to the action of the air in the furnace. The process is completed in four or five hours. The products consist of a regulus, called *coarse metal*, containing the greater part of the copper as sulphide and a certain quantity of sulphide of iron, and a slag rich in iron and containing numerous siliceous fragments disseminated through it, which give it a muddy consistence. This slag is raked out of the furnace by a rabble introduced through the door *p*, and falls into a series of

Fig. 133.



Fig. 134.



rectangular cavities *U*, formed in a bed of sand. At the same time, the melted coarse metal collected in the basin *B*, is run out by a tap-hole at the bottom into a reservoir *R*, containing water, whereby it is granulated.

The *coarse metal* contains about 33 per cent. of copper. It is brittle, and easily pulverised: its fractured surface is non-crystalline, uneven, more or less granular, generally vesicular, and of a bronze colour. The following analyses have been made of it by Leplay and by Napier.

*Composition of Coarse Metal.*

	Lepay (mean).		Napier.
Copper . . . . .	33.7	Copper . . . . .	21.1—39.5
Iron . . . . .	33.6	Iron . . . . .	33.2—36.4
Nickel, cobalt, manganese . . . . .	1.0		
Tin . . . . .	0.7		
Arsenic . . . . .	0.3		
Sulphur . . . . .	29.2	Sulphur . . . . .	45.5—25.0
Slag mechanically mixed . . . . .	1.1		
	99.6		

The slag, called *ore-furnace slag*, generally consists of a hard, brittle, black matrix, in which are imbedded sharp angular pieces of white quartz. It frequently contains small shots of coarse metal. If these are numerous, the slag must be remelted in subsequent operations. Its average composition, as determined by Lepay, is as follows:—

*Composition of Ore-furnace Slag.*

Quartz in admixture . . . . .	30.5
Silica in combination . . . . .	30.0
Alumina . . . . .	2.9
Protoxide of iron . . . . .	28.5
Lime . . . . .	2.0
Magnesia . . . . .	0.6
Various oxides (of tin, manganese, nickel, and cobalt) . . . . .	1.4
Fluorine . . . . .	1.0
Calcium . . . . .	1.1
Copper . . . . .	0.5
Iron . . . . .	0.9
Sulphur . . . . .	0.6
	100.0

This slag has nearly the composition of a ferrous metasilicate,  $\text{Fe}^2\text{SiO}_3$  or  $2\text{FeO} \cdot \text{SiO}_2$ .

It appears, then, that in the melting process in the ore-furnace, a considerable portion of the iron of the calcined ore is removed in the slag, and the whole of the copper, excepting the small portion which passes into the slag, is concentrated in a regulus containing, on the average, as much copper as pure copper pyrites (p. 22). The reduction of the sesquioxide of iron in the calcined ore to protoxide is due to the action of the sulphur, which is oxidised to sulphurous acid at the expense of the ferric oxide. Any copper that may exist in the state of silicate in the *metal slag*, forming part of the charge of the ore-furnace, is converted into cuprous sulphide by mutual decomposition with the sulphide of iron, which is always present in this furnace, and passes into the coarse metal.

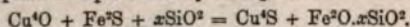
3. *Calcination of the granulated coarse metal.*—This operation is performed in a calciner, with free access of air, the charge being frequently stirred and turned over. The calcination is complete in about 24 hours, the heat being gradually raised towards the end of the process. No satisfactory analysis of the calcined product has yet been made. Lepay, however, found that, in a sample of coarse metal containing 33.7 per cent. copper, 34.2 iron, 1.5 of various other metals, 29.5 sulphur, and 1.1 slag, the proportion of sulphur was reduced by calcination to 16.4 per cent. The sulphur is evolved as sulphurous and sulphuric acids.

4. *Melting of the calcined coarse metal.*—The calcined product No. 3 is melted with addition of matters rich in oxide of copper, namely, *roaster and refinery slags*, and a quantity of ores of the fourth class (p. 24), consisting of oxides and carbonates of copper. The furnace is similar to the ore-furnace (fig. 133), excepting that the hearth has no basin. The process is conducted in a similar manner, excepting that it is continued two hours longer, and the heat is raised higher. The reaction consists mainly in a double decomposition between the sulphide of iron and oxide of copper, whereby oxide of iron is formed, which passes into the slag as silicate, and sulphide of copper, which forms the regulus; very little sulphurous acid is evolved. The slag is skimmed off, and drawn out of the furnace through the end opening below, where sand-beds are placed to receive it. The regulus is tapped off into sand-moulds immediately in front of and below the tap-hole of the furnace.

The composition of the regulus produced in this operation, varies with the proportion



of oxide of copper mixed with the calcined coarse metal. When a sufficient quantity of oxide and carbonate can be added to decompose the whole of the sulphide of iron present, the regulus has very nearly the composition of cuprous sulphide,  $\text{Cu}_2\text{S}$ , the decomposition taking place as represented by the equation —



The regulus formed under these circumstances is called *white metal*. It has a dark bluish grey colour, and faint metallic lustre, is compact and brittle, with uneven, granular, and more or less crystalline fracture. It contains on the average 73.2 per cent. copper. A sample analysed by Leplay, of specific gravity 5.70, contained 77.4 per cent. copper, 0.7 iron, with traces of nickel and cobalt, 0.1 tin and arsenic, 21.0 sulphur, and 0.3 slag and sand. Pure cuprous sulphide contains 80 per cent. copper. (See *SULPHIDES OF COPPER AND IRON*, ii. 77).

The slag, called *metal-slag*, is brittle, compact, and occasionally very crystalline, of blue-grey to bronze yellow colour, and inclining to metallic lustre. An analysis by Leplay gave:

Silica . . . . .	33.8	Magnesia . . . . .	0.3
Alumina . . . . .	1.5	Slag mechani- { Copper . . . . .	2.9
Protoxide of iron . . . . .	56.0	{ Iron . . . . .	0.3
Cuprous oxide . . . . .	0.9	{ Sulphur . . . . .	0.8
Various oxides . . . . .	2.1		
Lime . . . . .	1.4		100.0

If the proportion of oxidised copper-compounds in the charge is less than what is required for producing white-metal of the composition above given, the regulus will contain a considerable quantity of iron, constituting, from its colour, what is called *blue metal*; white-metal indeed passes insensibly into blue metal as the proportion of iron increases.

*Blue metal* always contains metallic copper diffused through it in very minute particles, and protruding into the interior of cavities in the mass, in delicate hair-like filaments. The manner in which this metallic copper is formed is not very clearly understood; but the reduction appears to take place during cooling, and to depend upon a reaction between the sulphide of copper in the regulus and the oxides in the slag. When the oxidised copper-compounds in the charge are in excess, some of the copper is likewise reduced, and a regulus is formed similar for the most part, in composition, colour, and properties, to white metal, but exhibiting on its upper surface numerous pimple-like excrescences, whence it is called *pimple-metal*.

5. *Roasting of the White or Blue metal*.—In this operation, the sulphur, which had hitherto been retained in union with the copper as an agent of concentration, is finally expelled in the form of sulphurous acid, and at the same time certain foreign metals, namely, arsenic, antimony, iron, cobalt, nickel, tin, &c., are removed, by conversion either into volatile oxides, or into silicates, which pass into the slag. The process consists of two successive reactions, which take place in the same furnace: 1. The direct action of the air on the metal kept at a temperature near its melting point; 2. The reaction of the oxide of copper thus formed on the sulphides not decomposed by the roasting, whereby sulphurous acid is evolved, and copper reduced to the metallic state. The metallic copper thus obtained is called *blister copper*, from the appearance of its surface. There is also formed a slag very rich in copper, called *roaster-slag*, which is added to the furnace-charge in the smelting of the calcined granulated coarse metal (No. 4).

The operation is performed in a reverberatory furnace similar to the melting furnace (*fig. 133*), but having a side door by which the pigs of regulus are introduced: and lateral openings near the fire-bridge for the admission of air. The rich oxidised ores of class 5 (ii. 24) are added to the charge. In half an hour, the pigs begin to melt, and the temperature is so regulated that the fusion may be complete in six or eight hours. The surface of the melted mass appears to boil, owing to the escape of sulphurous acid, produced by the mutual decomposition of the oxides and sulphides. The slag which forms on the surface of the melted regulus, is skimmed off twice during the operation, once immediately after fusion, and a second time just before tapping. After a while, the temperature of the furnace is lowered sufficiently to allow the regulus to solidify. When it has become pasty, its surface is thrown up into craters, in consequence of the continued evolution of gas, whereby the extent of surface exposed to the air is greatly increased and the oxidation assisted. Finally, the regulus is again melted into sand-moulds, where it solidifies in the form of *blister copper*.

The following are analyses of blister copper and roaster slag.



<i>Blister copper.</i>	<i>Lepay.</i>	<i>Napier.</i>		
Copper . . . . .	98.4	97.5	98.0	98.5
Iron . . . . .	0.7	0.7	0.5	0.8
Nickel, cobalt, manganese . . . . .	0.3	1.0	0.7	0.0
Tin and arsenic . . . . .	0.4	0.2	0.3	0.1
Sulphur . . . . .	0.2	0.6	0.5	0.6
	100.0	100.0	100.0	100.0

<i>Roaster slag.</i>	<i>Lepay.</i>
Silica . . . . .	47.5
Alumina . . . . .	3.0
Cuprous oxide . . . . .	16.9
Ferrous oxide . . . . .	28.0
Oxides of nickel, cobalt, manganese . . . . .	0.9
Stannous oxide . . . . .	0.3
Lime and magnesia . . . . .	traces
Metallic copper . . . . .	2.0
	98.6

According to Lepay, roaster-slag contains on an average 20 per cent. of copper, inclusive of that present in the metallic state. It is vesicular, more or less scoriaceous, of dark reddish-brown colour, varied here and there with greyish black, and without metallic lustre.

6. *Refining.*—This is the last operation, and its object is to remove the foreign metals and the remainder of the sulphur. The reagents by which this change is effected are, the oxygen of the air, and the siliceous matters of the hearth and walls of the furnace, together with those which are furnished by the sand adhering to the pigs of blistered copper. The refinery furnace is similar in construction to a melting furnace, excepting that the bottom inclines gradually from all sides towards the deepest part, which is near the end door, and there is a large door on one side, but neither a hole in the roof nor a side tap-hole. The furnace is charged with 6 or 8 tons of pigs of blistered copper, which are melted and exposed for about 15 hours, to the oxidising action of the air which enters the furnace. The oxide of copper formed, acts either immediately, or after combining with silica, on the sulphur and metals more oxidisable than the copper, thereby oxidising and causing them to pass into the slag, together with the excess of oxide of copper. The slag is skimmed off through the end opening.

The copper, thus freed from foreign metals and sulphur, is, however, in a peculiar state, being intimately mixed with a considerable quantity of red oxide, which destroys its malleability; in this state it is called *dry copper*. To deoxidise and *toughen* it, a quantity of anthracite, or free-burning coal—charcoal was formerly used—is thrown on the surface, and after a short time, a large pole of oak or birch, the greener the better, is thrust into it, and kept down by fixing a prop under the end which protrudes from the furnace. Under the influence of the high temperature, the wood gives off a large quantity of reducing gases, which cause the metal to boil violently, carrying the particles of carbon below its surface, and greatly accelerating the reducing action. After twenty minutes of this treatment, which is called *poling*, the refiner takes out a sample of the melted metal in a small ingot-mould, and when the ingot is cold, places it on an anvil, and tests its quality by hammering. As soon as it is found to possess the characters of good metal (*tough pitch*), the surface is again skimmed as fast as possible, and the metal ladled out into moulds. Should the metal, during the process of ladling, become more or less *dry* by oxidation, it is again poled for a short time. If, on the contrary, the poling has been continued too long, the copper again becomes brittle, probably because the oxides of certain other metals, lead, antimony, &c. present in small quantity, are reduced by the poling, and the copper consequently becomes alloyed with these metals; in this state it is said to be *overpoled*. To remedy this defect, the surface is uncovered, and exposed for a short time to oxidation. When the copper is intended for rolling, a certain quantity of lead may be advantageously added to it just before ladling. The proportion used is very variable, sometimes as much as 80 lbs. of lead to 6 tons of copper, sometimes not more than from 14 to 30 lbs.

The *refinery-slag* is very rich in copper. A specimen analysed by Lepay contained:

Silica . . . . .	47.4	Stannous oxide . . . . .	0.2
Alumina . . . . .	2.0	Lime . . . . .	1.0
Cuprous oxide . . . . .	36.2	Magnesia . . . . .	0.2
Ferrous oxide . . . . .	3.1	Shots of metallic copper . . . . .	9.0
Oxides of nickel, manganese, &c. . . . .	0.4		99.5

A specimen examined by Dr. Percy contained 57.9 per cent. copper existing as cuprous oxide, and 2.65 metallic copper; making a total of 60.55 per cent. copper.

It has already been observed, that when a plentiful supply of rich oxidised ores cannot be obtained, the calcinations and fusions have to be repeated a greater number of times: thus, instead of at once subjecting the white or blue metal resulting from the melting of the calcined coarse metal to the process of *roasting* (as above described), it is necessary, under such circumstances, to calcine it again, and subject the calcined product to an additional melting before commencing the roasting.

The *metal-slag* (No. 4), and likewise the *ore-furnace slag* when it contains numerous shots of regulus, are sometimes remelted in order to concentrate the regulus which they contain.

Lastly, we must notice the process of making what is called "best selected copper," which is merely a very pure metal used for fine purposes, especially for making the best brass. The process consists in melting one of the numerous varieties of *blue metal*, and tapping it into a series of moulds or sand-beds. The pigs nearest to the furnace then contain the greater portion of the metallic impurities, while those more remote contain a purer regulus, which is then roasted and refined. Another method is to roast the blue metal, or *pimple metal*, till about half the copper is reduced. The residual metal, called *regule*, *best regule*, or *spongy regule*, is afterwards roasted and refined by itself.

#### *Copper Smelting in Blast Furnaces.*

This is the method chiefly adopted on the continent of Europe, as in Sweden and in Germany.

*Swedish process.*—The Swedish copper ores, the principal mines of which are at Fahlun, in Dalecarlia, and Ätvidaberg, in Östergothia, consist of copper pyrites mixed with a large amount of iron pyrites and siliceous minerals.

1. *Roasting or Calcination.*—The ore is first *roasted* either in kilns formed by walls

Fig. 135.



built in the manner shown in *fig. 135*, or in open pyramidal heaps, most frequently the latter. In either case, a bed of wood about 12 inches high is formed on the ground, and on this the ore is piled in alternate layers with small charcoal, to the height of 2 or 3 feet in the kilns, and 10 or 12 feet in the heaps. By this means, a large portion of the sulphur is burnt away, while the iron is chiefly oxidised, as in the Welsh

process of calcination. The roasted ore should retain sufficient sulphur to furnish, when smelted, a regulus yielding from 20 to 30 per cent. of copper.

2. *Fusion of the roasted ore.*—The roasted ore is next mixed with *black copper slag* a product obtained in the fourth operation, and containing a large amount of iron. The proportions should be so adjusted as to yield, when smelted, a regulus containing from 20 to 30 per cent. of copper, and a slag having nearly the composition  $\text{Fe}^2\text{SiO}_3$ , or  $3\text{FeO} \cdot 2\text{SiO}_2$ , which is found to possess the proper degree of liquidity. The mixture of ore and black copper slag is smelted with coke, or a mixture of coke and charcoal in a cupola (*Schachtöfen*), called the *ore-furnace*, about 18 feet high, the fire being urged by a blast. The regulus obtained is a mixture or compound of the subsulphides of copper and iron.

3. *Roasting of the regulus.*—The regulus is next roasted in a range of kilns constructed on each side of a medium wall in the manner represented in *fig. 135*. The roasting is repeated four, five, or even six times. When the first firing is finished, the regulus is transferred to the next kiln, then to the next, and so on till it is roasted "dead" or "sweet." No charcoal is added in the first firing, but in the second  $1\frac{1}{2}$  measure of charcoal is spread upon the wood, and the quantity is increased in each successive firing, till, in the sixth, 12 measures of charcoal are added, forming three layers, including that on the wood. The entire roasting generally lasts from seven to eight weeks. During the roasting, oxide of zinc is formed from sulphide contained in the regulus.

*Fusion for black copper.*—The roasted regulus from the last operation is next smelted in the *black copper furnace*, which is also a cupola, but of smaller dimensions than the *ore-furnace*, in admixture with a roasted regulus (*thin regulus*) obtained in preceding operations, also with *refinery slags*, furnace-residues containing copper, and *ore-furnace slags*, sometimes also with addition of quartz. The products are *black copper* (*Schwartzkupfer*), an impure metallic copper, so-called from its superficial crust



of black oxide; *thin regulus*, containing from 55 to 72 per cent. of copper; and *black copper slag*, chiefly consisting of silicate of iron, but containing about 1 per cent. of copper. This slag is added to the charge of the ore-furnace in a subsequent operation, and the thin regulus is remelted in a subsequent fusion for black copper.

The black copper has lastly to be *refined*, to free it from sulphur and foreign metals. This is effected, as in the Welsh process, by melting it under a layer of charcoal, and subjecting it at the same time to the action of a current of air. The arrangements are similar to those used in Germany, which will be presently described.

The following are analyses of the *black* and *refined copper* of Åtvidaberg, made at the mining school of Fahlun:—

	Black copper.	Refined copper.
Copper . . . . .	94.39	99.460
Iron . . . . .	2.04	0.111
Zinc . . . . .	1.55	—
Cobalt and nickel . . . . .	0.63	0.110
Tin . . . . .	0.07	scarcely a trace
Lead . . . . .	0.19	ditto.
Silver . . . . .	0.11	0.065
Gold . . . . .	not looked for	0.0015
Sulphur . . . . .	0.80	0.017
Arsenic . . . . .	trace	
	99.78	99.7645

The greater part of the cobalt is separated in the refining, and becomes concentrated in the slag.

*Mansfeld process.*—The copper ore of the Mansfeld district in Prussian Saxony consists of argillaceous schists (*Kupfer-schiefer*), largely impregnated with bitumen, and containing copper pyrites disseminated in small crystals. The schist is first roasted in

Fig. 136.



Fig. 137.



pyramidal heaps on beds of wood. Very little fuel is required, the fire being kept up by the combustion of the bitumen contained in the schist. The roasted ore is then mixed with from 5 to 8 per cent. of fluor spar, cupriferous slag from subsequent stages of preceding operations, and often with small quantities of cupriferous schists containing carbonate of lime. This mixture is smelted in cupolas from 15 to 20 feet high, heated with coke. Fig. 136 is a vertical section of the furnace, passing through one of the *tuyeres*. Fig. 137 is a front view, with a section of the lower part of the shaft. This lower part of the crucible is formed of siliceous grit, the upper part of brick. The furnace (the ore-furnace) has two *tuyeres* *tt*,





placed either on the same side of the shaft (as in the figure), or on opposite sides. At the bottom of the crucible are two apertures, *o o'*, which are opened alternately to allow the fused products to run into the basins *C C'*. The furnace is filled with ore and fuel in alternate layers. The regulus and slag are constantly running from the furnace into one or other of the basins *C C'*. The slag is moulded into large bricks, which serve for building. The regulus (*Rohstein*), which does not amount to more than  $\frac{1}{10}$  of the weight of the roasted ore, is composed of cuprous sulphide,  $\text{Cu}_2\text{S}$ , and ferrous sulphide,  $\text{FeS}$ , and contains from 20 to 60 per cent. of copper, according to the nature of the ore. The poorer kinds of regulus containing from 20 to 30 per cent. of copper are roasted three times on beds of wood, and again smelted with slags from preceding operations, those being selected which lay immediately above the regulus in the basins *C C'*. A new regulus (*Spurstein*) is thus obtained, containing as large a proportion of copper as the first regulus of the richer ores.

The richer reguli (*Spurstein* and *Dünnstein*) are roasted six times in succession on beds of wood in kilns,—brick-walled kilns like those represented in *fig. 135* (p. 30). During the roasting a considerable quantity of sulphate of copper is formed, which is removed by lixiviation and crystallised.

The roasted and lixiviated regulus (*Gaarrost*) is now smelted with a due proportion of slag in a blast furnace, similar to that represented in *fig. 136*, but smaller. The products are *black copper*, a rich regulus (*Dünnstein*), which is added to the second regulus obtained in the preceding operation, and slag. The black copper is removed in the form of discs, by throwing water on the surface so as to form a solid crust. It contains about 95 per cent. of copper, 3 or 4 per cent. of iron, and small quantities of silver and antimony.

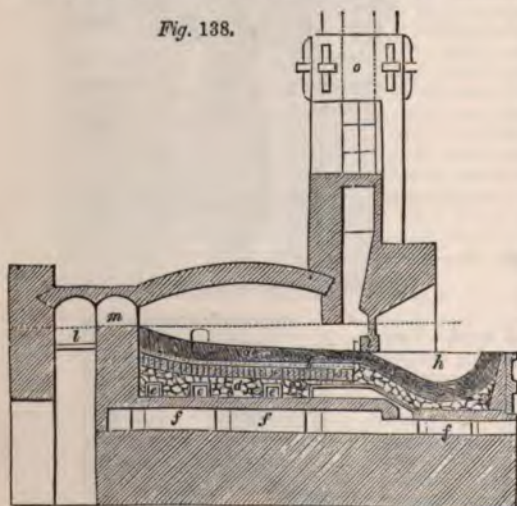
The quantity of silver in the black copper is generally sufficient to render its extraction profitable. This is effected by a process called *eliquation*, depending on the fact that lead forms with silver a more fusible alloy than with copper. The argentiferous copper is melted with lead (argentiferous lead, if it can be had), and the melted alloy is either suffered to cool very slowly, in which case the copper solidifies first in combination with a portion of the lead, while the rest of the lead, in combination with nearly the whole of the silver, remains liquid, or the whole of the fused mass is cast into discs, which are then subjected to a gradually increasing heat, the effect of which is to melt out the silver in combination with part of the lead, while an alloy of lead and copper remains in the solid state. The argentiferous lead is then cupelled to separate the silver. (See *SILVER*.)

The alloy of lead and copper thus obtained, still, however, retains a small portion of silver, which is sometimes separated from it by subjecting it to a higher temperature

in contact with a current of air, whereby a fresh portion of lead containing silver is separated, not, however, in the metallic state, but in the form of litharge.

*Refining.*—The black copper thus desilverised is refined in a reverberatory furnace constructed like a cupelling furnace.

The metal is fused on the hearth *a*, *fig. 138*, and subjected to the oxidising action of a blast of air from the tuyeres *n*, *fig. 139*. A red slag is then formed containing the foreign metals, iron, lead, &c., and a considerable quantity of cuprous oxide; it is removed from time to time by the door *p*. The refiner judges of the progress of the

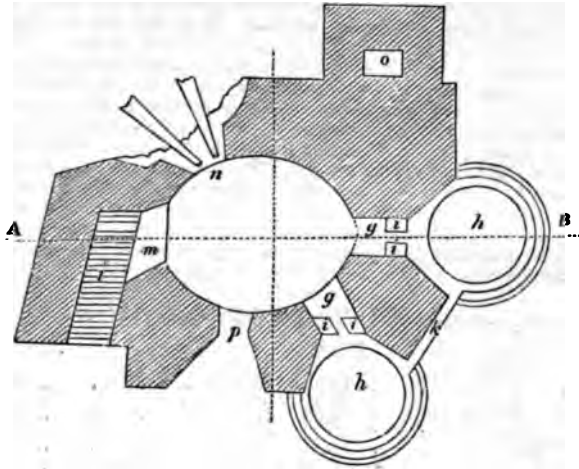


operation by taking out from time to time, a small quantity of the melted metal, and examining it in the manner to be presently described. When the process is finished, the melted copper is run off into the basins *h h*, and a little water is poured

upon it to form a crust on the surface, which is then taken off in the form of a disc called a *rosette*.

When the black copper does not contain silver, it is not subjected to the eliquation pro-

Fig. 139.



cess, but is immediately refined, in a small furnace, called a *refining hearth*, of which *fig. 140* is a vertical section and *fig. 141* is a perspective view.

It consists of a hemispherical crucible C, about 2 or 2½ feet in diameter, and 15 to 18 inches deep, and made of English fire-clay mixed with sand, and well beaten down. It is surrounded by a raised platform, having an opening A, which can be closed by a door.

Fig. 140.



Fig. 141.



The crucible having been dried by filling it with lighted charcoal, fresh charcoal is added, the pigs or discs of black copper are placed on the charcoal opposite to the tuyere T, and the blast is turned on. As soon as this portion of copper is melted, more is added, care being also taken to keep the crucible full of charcoal. A channel *i i*, allows the slag produced during the refining process to run off. As the oxidation proceeds, sulphurous acid is given off, sometimes accompanied by white vapours of oxide of antimony. The first portions of slag which run off are of a greenish colour, and contain much oxide of iron; the subsequent portions are of a dark red colour, and are rich in copper. To judge of the progress of the operation, the refiner from time to time dips a cylindrical iron rod into the melted copper, then quickly withdraws it, cools it by immersion in cold water, knocks off the hollow cylinder of copper adhering to the end, and examines it. If it is thick, smooth on the outer surface, and yellowish-red inside, the copper is "too young," and must be further exposed to the action of the blast. When it becomes thin, brownish-red, and crinkled on the outer surface, of a pure copper-red in the interior, with metallic lustre, and may be bent several times without breaking, the copper may be regarded as refined, or nearly so. When it becomes so thin as no longer to form a continuous coating, but merely to surround the iron in some places like network, and in others to present the appearance of small pointed or

bearded excrescences, the blast should be immediately stopped, as the copper is over-refined or "übergaar."

When the refining is judged to be complete, the copper is taken out in *rosettes* in the manner above described.

*Toughening (Hammergaarmachen).*—Rosette copper, though tolerably pure, is not very malleable, because it contains a considerable quantity of red oxide; in fact, it is in the state called "dry" by English smelters. It is sold for the manufacture of brass, and other purposes in which it requires to be melted up again. To convert it into malleable copper, it is again melted on a refining hearth, under charcoal, but with the tuyere less inclined than in the preceding process, so that the oxidising action of the blast may not be so strong. There is nothing peculiar in the process, excepting that it must be done with great care, so as just to reduce the oxide by the action of the red-hot charcoal, without bringing it into the *over-refined* state, like the over-poled copper of the English works (p. 29). The refiner takes out a sample now and then, and tests its qualities by hammering. Altogether the refining and toughening of the black copper is a more tedious process than that of the English *blister copper* (p. 29.) because the black copper is less pure than the latter.

The following analytical data in elucidation of the Mansfeld process are taken from *Percy's Metallurgy*:—

*Analyses of the Mansfeld Schist by Berthier.*

Unburnt.				Roasted.			
Silica . . . . .	40.0	Silica . . . . .	50.6	43.8			
Alumina . . . . .	10.7	Alumina } . . . . .	23.4	17.2			
Ferric oxide . . . . .	5.0	Magnesia } . . . . .					
Carbonate of lime . . . . .	19.5	Lime . . . . .	7.8	18.0			
Carbonate of magnesia . . . . .	6.5	Oxides, copper (Cu <sup>2</sup> O) . . . . .	2.8	2.5			
Copper pyrites . . . . .	6.0	Oxides, iron (Fe <sup>2</sup> O <sup>3</sup> ) . . . . .	9.0	7.2			
Potash . . . . .	2.0	Sulphur . . . . .	4.0	2.4			
Water and bitumen . . . . .	10.3	Loss by calcination . . . . .	0.8	6.0			
	100.0		98.4	97.1			

*Analyses of Ore-furnace Slags.*

	Heine.		Berthier.	Hoffmann.		Ebbinghaus.
Silica . . . . .	57.43	53.83	49.8	48.22	50.00	54.13
Alumina . . . . .	7.83	4.43	12.2	16.35	15.67	10.53
Lime . . . . .	23.40	33.10	19.2	19.29	20.29	19.41
Magnesia . . . . .	0.87	1.67	2.4	3.23	4.37	1.79
Ferrous oxide . . . . .	7.47	4.37	13.2	10.75	8.73	10.83
Oxide of zinc . . . . .				1.26	1.11	
Cuprous oxide . . . . .	0.30	0.24		0.75	0.67	2.03
Fluorine . . . . .	1.97	2.09	1.1			
Alkali (K <sup>2</sup> O), and loss			2.1			
	99.27	99.73	100.0	99.85	100.84	98.72

*Analyses of Ore Furnace Regulus (Rohstein).*

	Heine.				Rammelsberg.	
	a.	b.	c.	d.	e.	f.
Copper . . . . .	52.44	48.25	42.10	31.70	47.27	43.62
Iron . . . . .	20.49	17.35	19.25	28.75	19.69	23.35
Sulphur . . . . .	26.44	24.58	25.50	27.80	26.76	28.70
Zinc . . . . .		2.90	5.20	4.35		
Nickel } . . . . .						
Cobalt } . . . . .		0.80	1.05	1.25		3.45
Lead . . . . .	0.41	1.05	1.50	0.65		
Silver . . . . .	0.13	0.30	0.27	0.16		
Silica . . . . .		1.55	1.15	1.65	{ Zn, Ni, } { Co, Mn, } 4.09	
	99.91	96.78	96.02	96.31	97.81	100.00

{ Carbon,  
earthy  
matter,  
and  
loss. } 0.88



*Analyses of Concentrated Regulus (Spurstein), and Thin Regulus (Dünstein) from the Black-copper Furnace.*

	Spurstein.		Dünstein.			
	Ebbinghaus.	Berthier.	De la Trobe.	Schlesser.	Boujoukas.	
Copper . . . .	51.37	59.8	59.18	57.27	61.23	
Iron . . . . .	18.67	15.8	16.07	16.32	15.19*	
Sulphur . . . .	24.35	22.6	20.01	22.17	24.38	
Zinc, nickel, &c. .	6.54	.	2.97	2.55		
	100.93	98.2	98.23	98.31	100.80	

*Supposed Rational Constitution of the above (Rammelsberg).*

Cuprous sulphide . .	67.47	.	46.66	57.69	77.95
Ferrous sulphide . .	24.75	.	25.11	25.56	23.80
Sulphides of Zn and Ni . .	.	.	4.44	3.81	
Metallic copper . . .	5.98	.	21.96	10.08	traces

*Analyses of Slags accompanying Concentrated Regulus (Spurschlacke) and Black Copper.*

	Spurschlacken.		Black Copper Slag.		
	Wornum.	Hoffmann.	Berthier.	Ludi.	Gehrenbeck.
Silica . . . . .	33.18	34.11	33.6	38.15	37.90
Alumina . . . . .	11.22	8.46	5.6		
Ferrous oxide . . .	32.03	37.68	51.5	47.22	49.23
Lime . . . . .	17.14	13.38	5.0	11.56	9.07
Magnesia . . . . .	2.96	4.57	.	0.03	1.47
Copper existing partially as cuprous sulphide .	1.90	0.68	Cu <sup>2</sup> O 3.0	2.86	1.59
Sulphur . . . . .	not det.	0.46			
	98.43	99.34	98.7	99.92	99.26

*Analyses of the Completely Roasted Regulus (Gaar-röst).*

	Rammelsberg.	
Copper . . . . .	51.97	67.69
Iron . . . . .	20.39	10.56
Zinc and nickel . . .	—	0.67
Oxygen . . . . .	13.61	8.67
Sulphur . . . . .	2.11	1.64
Matter insoluble in acids .	11.92	9.49
	100.00	98.62

*Analyses of Black Copper.*

	Rammelsberg.		
	Berthier.	Hoffmann.	Ebbinghaus.
Copper . . . . .	95.45	89.13	92.83
Iron . . . . .	3.50	4.23	1.38
Lead . . . . .	.	0.97	2.79
Silver . . . . .	0.49	not determined	0.26
Zinc, nickel, and cobalt .	.	3.98	1.06
Sulphur . . . . .	0.56	1.07	1.07
	100.00	99.38	99.38

*Rivot and Phillips's Method of Copper Smelting.*

This method consists in completing the extraction of the copper by means of metallic iron, after the greater part has been separated by the ordinary process of reduction with coal or charcoal. Napier (Dingl. pol. J. xxvii. 293) had shown that copper may be precipitated from fused silicates containing it, by the action of the electric current, the mineral being fused in a black-lead crucible connected with the positive pole of the battery, and the negative pole being formed of an iron plate dipping into the fused mass. It was afterwards found, by numerous experiments made at the *École des Mines* in Paris, that metallic iron alone, without the aid of the battery, is capable of precipitating copper from silicates in a state of fusion, just as it does from

\* With other metals.

saline solutions at ordinary temperatures. In applying this method to practice, however, it was found that the expenditure of iron would be too heavy; hence the modification above noticed was adopted, of only using the iron to complete the reduction. The process is as follows: The ore is pounded, roasted in the calcining furnace, and then heated till all the sulphates are decomposed; by this means nearly all the sulphur is expelled. The roasted ore is then fused with lime and non-bituminous coal. The fusion, which must be quickly conducted, yields two products, viz. reduced copper at the bottom, and a fused mass of slag or silicate (called the *bath*) floating on the top; this contains the remainder of the copper, usually from 2 to 2½ pts. in a thousand (? in a hundred). This residual portion of copper is precipitated by the immersion of iron bars into the melted slag: the reduction occupies from three to four hours for a charge of 5 ctr. The slag, after this treatment, still retains from 0.005 to 0.0065 copper; the copper yielded by it is also contaminated with 0.004 iron and sulphur, and still requires refining. The estimated saving by this process, as compared with the ordinary method under given circumstances, is about 17 per cent. (Jahresb. d. Chem. i. 1021.)

#### *Extraction of Copper in the Wet Way: CEMENTATION COPPER.*

This method consists in precipitating copper from solution by metallic iron. It is not much practised, being economical only under peculiar circumstances. The drainage-water of mines in which the copper exists as sulphide, often contains sulphate of copper formed by oxidation of the pyrites. Solutions of copper are also prepared artificially by treating the poorer oxidised ores with sulphuric or hydrochloric acid, or by roasting pyritiferous ores, and extracting the sulphate by lixiviation (p. 32). Dr. Richardson, of Newcastle, exposes a mixture of pulverised copper pyrites and chloride of sodium or potassium, occasionally moistened with water (or salt-water may be directly used) to a temperature not lower than 80° F.; the copper is thereby converted into chloride, which is lixiviated with water. Ammonia has also been proposed as a solvent for extracting oxide of copper from the ores.

The precipitation is best effected by wrought iron; cast iron acts more slowly. The precipitation is accelerated by agitation, which has the effect of loosening a basic iron-salt which adheres to the surface of the metal, thereby exposing a fresh surface. The precipitated copper (*cementation copper*) is then melted and refined. This method is well adapted to the treatment of the poorer oxidised ores, like those of Twista in the Waldeck, especially where fuel is scarce.

According to Gaulthier de Claubry and Dechaud, the process may be accelerated and the consumption of iron diminished [? at the expense of zinc] by the use of a voltaic battery, the copper being likewise obtained in more coherent form. Copper is sometimes precipitated from its solutions in the metallic state without the use of iron, probably because the solution contains a cuprous salt, which splits up into a cupric salt and metallic copper.

The precipitation of copper from the solutions of its pure salts by electrolysis, as in the electrotype process, yields the metal in its state of greatest purity.

For further details on the metallurgy of copper, see *Percy's Metallurgy*, i. 289; *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 818; *Kerl's Hüttenkunde*, ii. 158; *Regnault's Cours de Chimie*, iii. 281.

#### *Impurities in Commercial Copper.*

A careful investigation of the nature and amount of the metallic impurities in numerous varieties of commercial copper, from various sources, has lately been made by Messrs. Abel and Field (Chem. Soc. J. xiv. 280), the general results of which are as follows:—

1. *Arsenic* and *silver* are almost invariable impurities in copper.
2. The occurrence of *bismuth* in copper is very general; this metal appears, indeed, to be always present, excepting when carbonates of copper have been used in the production of the metal, as in the Australian and Russian coppers. Field has shown (*ibid.* p. 304) that bismuth is of very common occurrence in copper minerals.
3. *Antimony* is not of so frequent occurrence in copper as is generally supposed; the bismuth existing in copper has doubtless often been mistaken for antimony, both these metals being precipitated by water from their acid solutions.
4. *Lead* is of very rare occurrence in cake-copper, but appears to be an almost invariable constituent of copper which has been manufactured into sheet or rod.
5. *Iron*, which, like sulphur, exists in considerable proportions in unrefined copper, is almost completely removed by the refining process.

The special results of the investigation are given in the following table:—

*Metallic impurities in different varieties of Copper.*

Description of Copper.	Silver.	Arsenic.	Antimony.	Bismuth.	Lead.	Tin.	Iron.
BAR AND BLISTER COPPER.							
Chile, No. 1 Bar	Silver was detected in all these specimens, but not determined.	traces	.	traces	.	.	0.62
" 2 "		traces	.	.	.	.	0.71
" 3 "		traces	.	traces	.	.	0.85
" 4 "		0.10	.	traces	.	.	0.91
" 5 "		traces	traces	traces	.	.	0.62
" 6 "		traces	.	traces	.	.	0.46
" 7 "		traces	.	traces	.	.	0.52
" 8 "		traces	.	traces	.	.	0.67
" 9 "		traces	.	traces	.	.	0.64
" 10 "		traces	traces	traces	.	.	0.52
" 11 "		traces	.	.	.	.	0.62
" 12 "		0.02	traces	.	.	.	0.50
" 13 "		0.04	traces	.	.	.	0.43
" 14 "		0.07	0.50	traces	.	.	0.51
" 15 "		.	.	.	.	.	0.84
" 16 "		0.40	traces	traces	.	.	1.64
" 17 "		0.45	.	.	.	.	1.52
" 18 "		traces	.	.	.	.	0.70
" 19 "		0.50	0.20	.	.	.	0.80
" 20 "		.	.	.	.	.	1.20
" 21 "		.	traces	traces	.	.	0.98
" 22 "		.	traces	traces	.	.	1.00
" 23 "		traces	.	traces	.	.	1.20
" 24 "		traces	.	traces	.	.	1.04
" 25 "		traces	.	traces	.	.	1.12
" 26 "		traces	.	traces	.	.	1.02
" 27 "		traces	.	traces	.	.	0.94
" 28 "		0.03	traces	traces	.	.	1.10
" 29 "		.	.	.	.	.	0.75
Blister Copper	0.10	traces	traces	.	.	0.32	
Matzacian Copper	traces	.	traces	.	.	1.32	
New Mexican	.	.	.	.	.	0.42	
Spanish, No. 1							
" 2 "	Silver was detected in all these specimens, but the quantities were not determined.	3.31	0.70	.	.	.	.
" 3 "		2.49	.	trace	.	.	.
" 4 "		2.15	.	0.04	trace	.	.
" 5 "		1.18	.	.	trace	.	.
" 6 "		1.20	.	.	.	.	.
" 7 "		0.90	.	.	.	.	.
" 8 "		0.30	.	.	.	.	0.21
" 9 "		0.25	.	.	traces	.	0.35
Swedish, No. 1	0.25	0.20	.	.	.	0.31	
Manilla Slab	1.24	traces	.	.	.	0.20	
Buenos Ayres Slab	0.31	0.65	0.05	.	.	.	
Australian (Sydney)	.	0.17	0.10	.	.	.	
" (Sydney)	.	.	.	.	.	1.01	
REFINED COPPERS.							
Chile, (Société Italienne)	Silver was detected in all these specimens, but the quantities were not determined.	.	.	.	.	.	0.01
Chile, No. 1		0.04	.	.	.	.	0.03
" 2 "		0.03	.	.	.	.	.
Spanish		traces	.	.	.	.	0.06
" No. 2.		0.63	.	.	.	.	.
Italian, No. 1.		.	.	.	trace	.	.
" 2.		.	.	.	trace	.	trace
Tuscan Rosette		.	.	.	minute traces	.	trace
Russian (CCND.)		0.11	.	.	.	.	.
" No. 2		.	.	.	.	.	.
Hungarian		0.36	0.22	traces	.	.	0.30
" Rosette		0.06	0.12	.	.	.	trace
Australian (Burra Burra)		0.02	.	.	.	.	trace
" (Kapunda)		0.01	.	.	.	.	trace
Lake Superior		0.07	0.01	.	.	.	trace
Norwegian (Alten)		trace	.	.	.	.	trace
North American		0.22	.	.	.	.	trace
" No. 2		0.06	.	.	.	.	trace
" 3		trace	.	.	.	.	trace
English Tile		traces	0.07	traces	0.02	.	trace
English Best Select, No. 1		0.03	0.03	.	0.05	.	trace
" 2		0.02	0.04	.	0.05	.	trace
" 3		0.02	0.01	.	0.04	.	trace
" 4		0.03	0.04	.	0.04	.	trace
" 5		0.02	0.12	0.02	0.05	.	trace
" 6		0.04	0.15	0.05	0.05	.	trace
" 7		0.03	0.14	0.02	0.04	.	trace
" 8		trace	0.13	0.07	trace	.	trace
" 9		trace	trace	trace	trace	.	trace
" 10		0.03	0.14	0.05	0.05	.	trace
" 11		0.07	0.31	trace	0.17	.	trace





formation of cuprous oxide, and its subsequent reduction by the charcoal, whereby carbonic oxide is produced, and, endeavouring to escape as the melted metal is about to solidify, forms cavities within it, and sometimes throws up the surface in vegetations. Copper, fused with free access of air and then cast in an atmosphere of coal gas, exhibited the same cavernous structure, the specific gravity of two portions thus cast being only 6.926 and 6.438, whereas two portions of the same fused metal cast in air had the specific gravities 8.618 and 8.665. Again, copper fused and left to cool under charcoal had a specific gravity of 8.952; the same cast in coal-gas, 8.929, whereas another portion of the same cast in air had a specific gravity of only 6.193.

Sulphur acts in the same manner as charcoal. The density of vesicular copper is greatly increased by hammering, but that of copper not possessing the vesicular structure is but little increased even by very powerful pressure. Marchand and Scheerer found that the density of copper fused under common salt was increased by a pressure of 300,000 lbs. only from 8.921 to 8.930.

The *cubical expansion* of copper by heat for  $1^{\circ}$  C. is 0.000051 (the volume at  $0^{\circ}$  C. being taken as unity), hence the *linear expansion* is 0.000017 (H. Kopp, Ann. Ch. Pharm. lxxxi. 1); according to Troughton, it is 0.000019188.

*Specific heat* = 0.09516, between  $0^{\circ}$  and  $100^{\circ}$  C. (Regnault.)

Copper melts more easily than gold, less easily than silver. According to Pouillet, therefore, its melting point is between  $1000^{\circ}$  and  $1200^{\circ}$  C.; according to Guyton-Morveau, it is  $1207^{\circ}$  C. ( $2204^{\circ}$  F.); according to Daniell,  $1398^{\circ}$  C. ( $2538^{\circ}$  F.). All these determinations of very high temperatures are liable to great uncertainty. It expands on solidifying. Copper containing red oxide melts at a lower temperature than pure copper, but does not form so thin a liquid; it likewise solidifies more slowly. If the proportion of oxide is larger, the mass does not expand in solidifying. The expansion is also prevented by an admixture of 0.1 per cent. of potassium, zinc, or lead. Copper containing carbon behaves in the fused state like pure copper.

*Electric Conductivity.*—Copper possesses great power of conducting heat and electricity, standing in this respect next to silver. Its electric conductivity has been studied with great care by Matthiessen and Holzmänn (Phil. Trans. 1860, pt. i.; see also Matthiessen, Proc. Roy. Soc. xi. 126), who have examined particularly the effect produced upon it by the presence of foreign substances, a subject of great importance with reference to the use of copper wires for electro-telegraphy. The results are given in the following table:

*Electro-conductivity of Copper, that of a hard-drawn Silver wire being = 100.*

Wires hard drawn.	How prepared.	Conducting power.	Temperature. C.
1. Pure copper	Protoxide reduced by hydrogen	93.00	at $18.6^{\circ}$
2. "	Electrotype copper not melted	93.46	" 20.2
3. "	commercial "	93.02	" 18.4
4. "	No. 3. After fusion in hydrogen	92.76	" 19.3
5. "	No. 3. Hydrogen passed through the metal while melted	92.99	" 17.5
Mean of the twelve determinations from which the preceding numbers were deduced.		93.08	" 18.9
Extremes observed.		92.22	" 19.3
and		93.81	" 19.7

The conducting power was found to be increased about 2 per cent. by annealing the wires.

6. Copper containing red oxide, melted in contact with air		73.32	" 19.5
7. "	2.60 per cent. of phosphorus	7.24	" 17.6
8. "	0.95 "	23.24	" 22.1
9. "	0.13 "	67.67	" 20.0
10. "	6.40 " arsenic	6.18	" 16.8
11. "	2.80 "	13.14	" 19.1
12. "	traces "	57.80	" 19.7
13. " alloyed with	3.20 " zinc	56.98	" 10.3
14. "	1.60 "	76.35	" 15.8
15. "	traces "	85.05	" 19.0
16. "	1.06 " iron	26.95	" 13.1
17. "	0.48 "	34.56	" 11.2
18. "	4.90 " tin	19.47	" 14.4
19. "	2.52 "	32.64	" 17.1
20. "	1.33 "	48.52	" 16.8
21. "	2.46 " silver	79.38	" 19.7

		Conducting power.	Temperature C.
22.	Copper alloyed with 1.22 per cent. of silver	86.91	at 20.7
23.	" " 3.50 " gold	65.36	" 18.1
24.	" " { 0.31 " antimony } { 0.29 " lead }	64.5	" 12.0
25.	Electrotype copper, from a dense ingot melted under charcoal and cast in coal gas (ii. 39)	93.2	" 12.8
26.	Electrotype copper from a porous ingot of the same copper melted in the ordinary way	94.8	" 13.0
27.	Electrotype copper cemented with charcoal and containing silicon and traces of phosphorus and iron.	62.8	" 13.0
	Ditto. ditto.	63.2	" 14.2

These results show that the electric conductivity of copper is very greatly impaired even by small quantities of foreign substances. The conducting power of perfectly pure copper is estimated by Matthiessen as = 96.4 at 13° C.

The following table exhibits the conducting power of various kinds of commercial copper as compared with that of pure unmelted electrotype copper, which is taken as the standard, and as equal to 100 at 15.5° C.

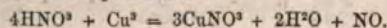
Wires annealed.		Conducting power.	Temperature C.
1.	Spanish (Rio tinto), containing 2 per cent. arsenic, besides traces of lead, iron, nickel, red oxide, &c.	14.24	at 14.8°
2.	Russian, (Demidoff's make), containing traces of arsenic, iron, nickel, red oxide of copper, &c.	59.34	" 12.7
3.	Tough-cake (make not specified), containing traces of lead, nickel, antimony, red oxide of copper, &c.	71.03	" 17.3
4.	Best selected (make not specified), containing traces of iron, nickel, antimony, red oxide of copper, &c.	81.35	" 14.2
5.	Australian, Burra Burra. Traces of iron and red oxide of copper only were found.	88.86	" 14.0
6.	American, Lake Superior, containing traces of iron and red oxide of copper, and 0.03 per cent. silver.	92.57	" 15.0

*Finely divided copper.*—Copper may be obtained in this state: 1. By reducing the carbonate at a very gentle heat in an atmosphere of hydrogen (Osann, Pogg. Ann. lii. 406). 2. By boiling a concentrated solution of sulphate of copper not containing free acid, with distilled zinc. As soon as the liquid loses its colour, which it does in a short time, the zinc is removed, and the copper powder well boiled with dilute sulphuric acid, then washed uninterruptedly with water, pressed between bibulous paper, and dried at 75° C., or in a warm retort through the tubulure of which a stream of hydrogen is passed (Böttger, Ann. Ch. Pharm. xxxix. 172). 3. By igniting a mixture of 5 pts. cuprous chloride and 6 dry carbonate of sodium with sal-ammoniac, and afterwards exhausting with water. (Wöhler and Liebig, Pogg. Ann. xxi. 583). Copper thus prepared is a soft, dark-red, dull looking powder, which easily acquires the ordinary lustre of the metal by pressure, and if pressed together while red-hot welds together into a compact mass.

#### *Chemical properties of Copper.*

Copper has much less affinity for oxygen than iron, and decomposes water only at a bright red heat and to a small extent. In dry air it remains unaltered at ordinary temperatures, but oxidises rapidly at a red heat. In damp air it acquires a green coating of basic carbonate, and its oxidation is remarkably promoted by the presence of acids. The weaker acids, such as acetic acid, have no effect on copper, unless assisted by the oxygen of the air, when the copper rapidly combines with the oxygen and a salt of the acid is formed (see ACETATES OF COPPER, i. 14). Copper does not dissolve in cold *hydrochloric acid*; but when boiled with that acid, especially in the finely divided state, it displaces hydrogen, and slowly dissolves as hemichloride  $\text{Cu}^2\text{Cl}$  (Vogel, Schw. J. xxxii. 301; Odling, Chem. Soc. Qu. J. ix. 291.)

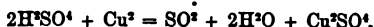
*Nitric acid* of ordinary strength acts violently on copper, with copious evolution of nitric oxide and formation of cupric nitrate:





But the *strongest nitric acid* (specific gravity 1.52) does not act on copper, the metal when immersed in it remaining bright and quiescent; probably the action begins in the manner just described, and an extremely thin film of nitrate is formed on the surface of the metal, which being insoluble in the strong acid, stops the further action. The same *passive* state is exhibited by other metals when immersed in strong nitric acid, especially by iron (*q. v.*) On diluting the acid with water, a violent action is instantly set up.

*Nitro-muriatic acid* dissolves copper with facility, forming cupric chloride. Copper is not attacked by *dilute sulphuric acid*, or even by *strong sulphuric acid* at common temperatures, but on applying heat, sulphurous anhydride is evolved and sulphate of copper is produced :



This at least is the principal reaction which takes place; but a portion of the sulphuric acid suffers more complete decomposition, sulphur being deposited, part of which remains in the free state, while the rest unites with the copper as sulphide.

Copper likewise oxidises in *alkaline* and in *saline solutions* exposed to the air. In a dilute solution of *ammonia* exposed to the air, it is converted into cuprous oxide and dissolves.

Copper in the state of foil or filings takes fire in *chlorine gas* at ordinary temperatures. At a red heat, it unites directly with *bromine, iodine, sulphur, selenium, silicon*, and all the metals; with *mercury* at ordinary temperatures. With *carbon* and with *nitrogen* it does not appear to unite directly, even at a red heat.

#### Compounds of Copper.

Copper forms two classes of compounds, the *Proto-compounds*, or *Cupric compounds*, containing 1 at. of the metal united with 1 at. of a monatomic radicle, or 2 at. metal with 1 at. of a diatomic radicle; *e. g.*  $\text{CuCl}$ ,  $\text{Cu}(\text{NO}_3)$ ,  $\text{Cu}^2\text{O}$ ,  $\text{Cu}^2\text{SO}_4$ ; and *Hemi-compounds*, or *Cuprous compounds* (commonly called *di-compounds*), containing 2 at. copper with 1 at. of a monatomic radicle, or 4 at. copper with 1 at. of a diatomic radicle, *e. g.*  $\text{Cu}^2\text{Cl}$ ,  $\text{Cu}_2\text{O}$ , &c. The cupric compounds may be supposed to contain the radicle *Cupricum*,  $\text{Cu} = 31.6$ ; and the cuprous compounds, the radicle *Cuprosium*,  $\text{Cu} = 73.2$ , their formulæ then becoming  $\text{CuCl}$ ,  $\text{Cu}_2\text{O}$ , &c. There are also a few compounds containing copper united with electro-negative radicles in other proportions, *e. g.* a nitride,  $\text{Cu}^*\text{N}$ , or perhaps  $\text{Cu}^*\text{N}$ .

**COPPER, ALLOYS OF.** Copper unites easily with most other metals. Many of the alloys were formerly stated to be chemical compounds formed in atomic proportions, but it is most probable that all of them (excepting those of copper and arsenic, which element occupies an intermediate place between metals and metalloids) are merely homogeneous mixtures.

The presence of small quantities of foreign metals, as arsenic, bismuth, zinc, iron, &c., in copper, produces considerable modification of its physical properties, for the most part impairing its malleability, tenacity, power of conducting heat and electricity, &c.

1. With **Aluminium**. (See i. 155).

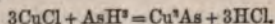
2. With **Antimony**. An alloy obtained by fusing the metals together in equal quantities is of a pale violet colour, very brittle, and of laminar structure. According to Karsten, copper alloyed with 0.15 per cent. antimony is brittle when cold, and very brittle at a red heat.

3. With **Arsenic**. An arsenide of copper,  $\text{Cu}^*\text{As}$ , occurs native, as *Domeykite*, in the copper mines of Coquimbo and Copiapo in Chili, and in some Cornish mines, in reniform and botryoidal shapes, also massive and disseminated. Hardness, 3 to 3.6; lustre, metallic; colour, tin-white, with slightly yellowish or iridescent tarnish; fracture, uneven. Specimens from Chile, analysed by Domeyko, gave: 1. From Calabazo, 28.36 per cent. As, and 71.64 Cu. 2. From Copiapo, 23.29 As, 70.70 Cu, 0.52 Fe, and 3.87 S = 98.28. The formula  $\text{Cu}^*\text{As}$  requires 28.3 As, and 71.7 Cu. The Cornish mineral *Condurrite* (*q. v.*) appears to be a mixture of Domeykite with red copper ore, arsenious acid, and arsenate of copper.

Alloys of copper and arsenic may be formed by melting the two metals together, in which case, however, there is considerable loss of arsenic by volatilisation;—or by heating copper with arsenious acid and charcoal, or other carbonaceous matter; or by heating an arsenite or arsenate of copper with charcoal. The alloy called *white copper*, or *white tombac*, which has nearly the composition  $\text{Cu}^*\text{As}$ , is obtained in this manner. Percy (*Metallurgy*, i. 281) describes an experiment in which an intimate mixture of 500 grs. of copper, 1000 grs. of arsenious acid, 1000 grs. of carbonate of sodium, and 500 grs. starch, exposed to a strong red heat, yielded a hard, brittle alloy, having a crystalline and dark bluish-grey fracture, melting before the blow-pipe below a red heat, and evolving copious arsenical fumes. It was

found to contain 34·2 per cent. arsenic, which is rather more than the amount indicated by the formula  $\text{Cu}^3\text{As}$  (66·2 Cu + 33·8 As). Berthier (*Traité des Essais par la voie sèche*, ii. 410) describes an alloy obtained by melting 1 pt. of the tetra-cupric arsenide,  $\text{Cu}^4\text{As}$ , with 4 pts. of copper, as semi-ductile, reddish-grey, with a slightly fibrous fracture, and susceptible of a fine polish.

*Tricupric arsenide*, or *Tricupraraine*,  $\text{Cu}^3\text{As}$  (analogous to  $\text{NH}^3$ ,  $\text{PH}^3$ ,  $\text{AsH}^3$ , &c.), is produced by passing arsenetted hydrogen gas over dry chloride of copper, or into a solution of cupric sulphate :



It is a black substance. (Kane, Pogg. Ann. xlv. 471.)

Copper alloyed with 0·15 per cent. arsenic, becomes somewhat brittle when cold, and very brittle at a red heat.

The arsenides of copper, fused with nitre in proper proportion, yield arsenate of potassium and metallic copper free from arsenic. Heated with oxide or arsenate of copper, they give off arsenious oxide, and yield metallic copper. A mixture of 10 pts.  $\text{Cu}^3\text{As}$  and 6 pts.  $\text{Cu}^2\text{O}$  yields, when heated, 10·9 pts. copper; and a mixture of 10 pts.  $\text{Cu}^4\text{As}$  with 6 pts. tetra-cupric arsenate  $\text{Cu}^4\text{As}^2\text{O}_7$  yields about 9·2 pts. copper, supposing the operation to be performed in perfectly closed vessels. When the fusion is effected in an open crucible, part of the arsenic is roasted by atmospheric oxidation, and less oxide or arsenate of copper is required to render the metal pure. (Berthier.)

4. With **Bismuth**. The two metals unite at a temperature below the melting point of copper. An alloy of 1 pt. copper and 2 pts. bismuth begins to expand a considerable time after solidification (Marx, Schw. J. lvi. 470). Copper alloyed with small quantities of bismuth remains ductile at mean temperatures, but when hammered becomes so hard and brittle as to require a second ignition, and if the quantity of bismuth exceeds 0·6 per cent., the alloy cracks on the edges when hammered at a red heat (Karsten). Bismuth is a frequent impurity in metallic copper (p. 36).

5. With **Cadmium**. An alloy containing 54·29 pts. copper and 45·71 cadmium has a light yellowish white colour, a fine-grained scaly structure, and is very brittle. The cadmium volatilises completely when the alloy is heated to the melting point of copper. Even a small quantity of cadmium renders copper brittle. (Stromeyer.)

6. With **Gold**. (See GOLD.)

7. With **Iridium**. (See IRIDIUM.)

8. With **Iron**. Combination between copper and iron takes place with difficulty.—100 pts. of copper may be made to unite by fusion with any quantity of bar-iron from 1 pt. to 100 and upwards. The intensity of the copper colour increases till the quantities of the two metals become equal; but the more the quantity of the iron exceeds that of the copper, the paler does the alloy become on the fractured surface. The alloy of 2 pts. copper to 1 pt. iron has the greatest tenacity; if the proportion of iron be increased, the hardness increases but the tenacity diminishes, and the fracture then becomes laminar. From ores containing the sulphides of iron and copper, the following alloys containing different proportions of the two metals may be prepared. One alloy of this kind was copper-red on the outer surface, had a pale uniform fracture, and was magnetic. Another exhibited externally a copper-red colour inclining to grey, had a deep copper-coloured and laminated fracture, was magnetic, and interspersed with isolated granules of copper and a few granules of iron. A third was iron-coloured, hard, had a laminar fracture, was strongly magnetic, and exhibited isolated granules of copper and numerous granules of iron. (Mushet, Phil. Mag. [3] vi. 81.)—According to former statements, the alloy of copper and iron is grey, slightly extensible, more difficult to fuse than copper, and magnetic even when it contains only  $\frac{1}{10}$  pt. of iron. The brittleness of iron at a red heat appears sometimes to proceed from admixture of copper.

Carbon interferes with the combination of iron and copper. Copper impairs the quality of steel; and in the proportion of 2 per cent. renders it brittle. (See IRON, CARBURET OF.)

9. With **Lead**. The two metals fuse together at a strong red heat, but the mixture, unless cooled very rapidly, separates into two alloys, the lower consisting of cuprif-erous lead, the upper of plumbiferous copper. By rapid cooling, an apparently homogeneous mixture may be obtained, but on heating it again, the compound containing the larger proportion of lead fuses out, while that which contains the larger proportion of copper remains; this is the principle of the eliquation process (p. 32).

Small quantities of lead diminish the ductility of copper, both at common temperatures and at a red heat. Copper containing 0·1 per cent. lead may be used for ordinary purposes, but cannot be formed into thin leaves or wires; that which contains 0·3 per cent. lead works better cold than hot, as in the latter case it cracks immediately at the edges. (Karsten.)

Lead enters into the composition of many ancient bronzes, sometimes in large proportion; see Tables B and D, pp. 45, 50.

10. With **Manganese**. Reddish white, very malleable, acquires a green tarnish by exposure to the air.

11. With **Mercury**. See **MERCURY**.

12. With **Molybdenum**. Pale, copper-coloured alloy; malleable if the molybdenum is not in excess.

13. With **Nickel**. The alloys are very extensible, and incline to white in proportion to the quantity of nickel: 10 pts. copper with 1 pt. nickel form a pale copper-red alloy, perfectly ductile; 10 pts. copper to 2 nickel, reddish white; 10 copper to 3 nickel, almost white; 10 copper to 4 nickel perfectly white, exhibiting on the touchstone the whiteness of silver. (Frick, Schw. xlviii. 114.)

Old slags from disused mines at Suhl contain white granules of metal, which are extracted and sold as Suhlman nickel silver (*Suhler Weiss-Kupfer*). According to Brandes, Schw. J. xxxix. 17, this alloy contains 88 per cent. copper, 8.75 nickel, 0.75 sulphur and antimony, and 1.75 iron, silicon, and aluminium.

For the alloys of copper, nickel, and zinc, see p. 51.

14. With **Platinum** and the allied metals. (See those metals.)

15. With **Potassium**. According to Serullas, copper heated to redness with cream of tartar does not become alloyed with potassium. According to Karsten, copper thus treated takes up a quantity of potassium not exceeding 0.13 per cent., and is thereby rendered somewhat less ductile when hot.

16. With **Silver**. See **SILVER**.

17. With **Tin**. The alloys of tin and copper are of great importance, constituting bronze, gun-metal, and bell-metal. The following details are taken from *Gmelin's Handbook* (v. 481).

The arms of the ancients were sometimes made of bronze, an alloy formed of a large quantity of copper with a little tin. It is obtained by fusing the two metals together, generally in a reverberatory furnace; if the mixture is not stirred, two distinct strata are apt to form, containing very different proportions of the constituent metals. The combination of the metals in equal parts takes place without evolution of light and heat. (Gehlen.)

TABLE A.—*Properties of Alloys of Copper and Tin*, according to Mallet (Dingl. polyt. J. lxxxv. 378).

1 at. copper = 31.6, and 1 at. tin = 58.9.

At.* Cu. Sn.	Per cent. Cu.	Spec. Grav.	Colour.	Fracture.	Tenacity.	Order of Mal- leability.	Order of Hard- ness.	Order of Fusil- bility.
1 : 0	100	8.607	.	.	24.6	1	10	16
a. 10 : 1	84.29	8.561	r. y.	f. gr.	16.1	2	8	15
b. 9 : 1	82.81	8.462	r. y.	f. gr.	15.2	3	5	14
c. 8 : 1	81.10	8.469	y. r.	f. gr.	17.7	4	4	13
d. 7 : 1	78.97	8.728	y. r.	v. c.	13.6	5	3	12
e. 6 : 1	76.29	8.750	pale r.	v.	9.7	brittle	2	11
f. 5 : 1	72.80	8.575	pale r.	c.	4.9	brittle	1	10
g. 4 : 1	68.21	8.400	ash-gr.	c.	0.7	friable	6	9
h. 3 : 1	61.69	8.539	dark gr.	lam. gr.	0.5	friable	7	8
i. 2 : 1	51.75	8.416	grey w.	v. c.	1.7	brittle	9	7
k. 1 : 1	34.92	8.056	whiter	lam. gr.	1.4	brittle	11	6
l. 1 : 2	21.15	7.387		v. gr.	3.9	brittle	12	5
m. 1 : 3	15.17	7.447	still	v. gr.	3.1	8 tough	13	4
n. 1 : 4	11.82	7.472	whiter	v. lam.	3.1	6 tough	14	3
o. 1 : 5	9.68	7.442		earthy	2.5	7	15	2
0 : 1	0	7.291	.	.	2.7	.	16	1

In this table, *r.* under *Colour*, denotes red, *y.* yellow, *gr.* grey. Under *Fracture*, *f. gr.* denotes fine-grained, *c.* conchoidal, *v.* vitreous, *lam.* laminar. The numbers under *Tenacity*, denote the weight in tons required to break a rod whose transverse section measures a square inch. The malleability was determined at 60° F. (15.6 C.) Under *Hardness* and *Fusibility*, the number 1 denotes the minimum. *a*, *b*, and *c* are gun-metal; *d*, is hard brass for pin-makers; *e* to *i* are bell-metal; *k* and *l*, bell-metal for small bells; *m*, *n*, and *o*, speculum-metal. (Mallet.)

\* The "atoms" in this column and in the corresponding column of Table C (p. 47) must be understood as merely indicating proportions; the alloys are not definite compounds.



a. Copper, alloyed with a very small quantity of tin, becomes so hard and brittle when hammered cold, that it requires to be again heated to full redness. (Karsten.)

b. 32 pts. copper to 1 tin: resists the solvent action of hydrochloric acid much more completely than pure copper, and is therefore adapted for the sheathing of ships. (Mushet, Phil. Mag. [3] vi. 444.)

c. 19 pts. copper to 1 tin: golden yellow, hard, malleable.

d. From 8 to 11 pts. copper to 1 tin: yellow and slightly malleable: *Gun-metal*. The best proportion appears to be 9 pts. copper to 1 tin. The alloy of 11 pts. copper to 1 tin appears uniform after sudden cooling, to the unassisted sight; but when examined with a lens, it appears to be composed of striated faces of a reddish alloy mixed with a white one. If it be still more rapidly solidified by pouring it into thick iron moulds, an alloy is obtained which appears perfectly uniform, even under the lens. When quickly cooled in water after continued strong ignition, it remains uniform; but if suffered to cool slowly after continued ignition, it becomes variable in composition, like that which has been slowly cooled after fusion. Hence the alloy which is uniform at the melting heat, and likewise at a strong red heat, separates into two different alloys when slowly cooled. The large mass of a cannon cannot be cooled, even by moulds which conduct heat well, suddenly enough to prevent the formation of two distinct alloys, the one that is richer in copper solidifying first, while that which is richer in tin, containing 82.3 per cent. copper to 17.7 tin, partly rises to the top, and partly sinks into the mould. (Karsten, Schw. J. lxx. 387.)

e. 6.25 pts. copper to 1 tin: the densest of all the alloys; its specific gravity is 8.87. (Briche.)

f. From 4 to 5 pts. copper to 1 tin: *Bell-metal*. Yellowish-grey, and, when very slowly cooled from a red heat, very hard, difficult to file, sonorous, brittle, exhibiting a fine-grained fracture. When heated to redness, and then suddenly cooled by immersion in water, it becomes soft, and easy to file and turn, but may be hardened again by ignition and slow cooling. The Chinese cymbals called *Gong-gongs* are made of this alloy (D'Arcet, Gilb. Ann. lvi. 104; further Ann. Ch. Phys. liv. 331). Bell-metal becomes malleable at a temperature not far below redness (Wollaston, Gilb. Ann. lvi. 106).—An alloy of 4 pts. copper and 1 tin fused, and then very slowly cooled, exhibits a striated surface, a dingy white close fracture, and is very brittle. When poured out into cold iron moulds, it exhibits the same properties; but if immersed in cold water, after being kept for some time at a low red heat, it becomes yellowish-white and extensible. During the ignition, if somewhat too strong, white globules of an alloy richer in tin are seen to ooze out, but at a higher temperature, when the whole mass becomes liquid, they disappear. Hence the alloy appears to be resolved at a temperature below its melting point, into two other compounds, which, on slow cooling, reunite and form a brittle alloy, but remain separated if the cooling be more sudden.

g. 3 pts. copper to 1 tin: reddish-white; very brittle; specific gravity 8.879 (Chaudet). With a small quantity of arsenic it forms a *speculum-metal*. (Little.)

h. 2 pts. copper to 1 tin: steel-grey, very hard. Remains uniform, even after slow cooling from a state of fusion (Karsten).—2 pts. copper, 1 tin, and  $\frac{1}{10}$  arsenic, form a *speculum-metal*; so likewise do 62 pts. copper, 33 tin, 2.5 arsenic, and 8 brass. (Little.)

i. 1 pt. copper to 1 tin: bluish-white, like zinc; slightly malleable, not very hard; specific gravity 8.468 (Chaudet), 8.79 (Briche). Remains uniform after slow as well as after sudden cooling. (Karsten.)

k. 1 pt. copper to 2 tin: white; brittle. Uniform, even after slow cooling. (Karsten.)

l. 1 pt. copper to 3 tin: bluish white, exhibits a crystalline aspect and fibrous texture; cracks under the hammer. Specific gravity 7.813. (Chaudet.)

m. 1 pt. copper to 3.6 tin. In a tinned copper boiler, regular six-sided prisms were found to be formed, with indistinct cleavage parallel to *p* (Miller, Phil. Mag. [3] vi. 107). Yellow-greenish-white; shining; ductile; of specific gravity 7.53; fusing at a red heat; slowly attacked by dilute, easily by strong nitric acid; dissolves rapidly in boiling hydrochloric acid. (Gives by analysis 21.38 per cent. copper, and 77.63 tin, which agrees nearly with the formula  $\text{CuSn}^2$  (31.33 Cu and 78.67 Sn). (Roth, Pogg. Ann. xxxvi. 478.)

n. 1 pt. copper to 10 tin: malleable to a certain extent, but cracks under the hammer; specific gravity 7.472. (Chaudet.)

Boiling hydrochloric acid extracts tin from these alloys, and leaves a compound containing a large quantity of copper with a small quantity of tin. (Chaudet, Ann. Ch. Phys. vii. 275.)

The following table exhibits the composition of numerous bronzes, ancient and modern. Some of them contain larger quantities of zinc and lead than of tin, but they are placed here for the sake of comparison with the rest. See also Table D (p. 50).

TABLE B.—Composition of Bronze Coins, Weapons, Parts of Machinery, &amp;c.

	Authority.	Spec. Gr.	Copper.	Tin.	Zinc.	Lead.	Iron.	
1. Old Attic coin*	A. Mitscherlich	88.46	10.04			1.05		
2. Athenian	Mits. & Schmid	76.41	7.05			16.54		
3. "	R. Wagener	83.62	10.85			5.53		
4. Coin of a Macedonian king	O. Monse	87.95	11.44					
5. Coin of Alexander the Great.	E. Schmid	95.96	3.28			0.76		Gold trace
6. Coin of Alexander the Great.	R. Wagener	86.76	10.24			2.31		"
7. Attic coin	Marchand	87.89	11.58				0.27	
8. " "	"	88.81	9.61				1.18	
9. Of Aug. Domit. Cons.	"	88.8	10.3			0.9		
10. Nerva Trajan.	"	85.1	11.5			3.4		
11. Marcus Antoninus	"	84.9	10.5			4.6		
12. Marc. Aurel. Commodus.	"	89.5	9.6			0.9		
13. Alexander Severus.	"	89.0	10.2			0.8		
14. Phil. Augustus	"	88.8	8.0			3.2		
15. Roman As, n.c. 500 <sup>b</sup>	Phillips	8.59	69.69	7.16		21.82	0.47	
16. Semis, n.c. 500	"	8.64	62.04	7.66		29.32	0.18	
17. Quadrans, n.c. 500	"	8.58	72.22	7.17		19.56	0.40	
18. Hiero, n.c. 478	"	8.72	94.15	5.49			0.32	
19. Alex. the Great, n.c. 335	"	8.69	86.77	12.99				
20. Philip III. of Macedon n.c. 323	"	8.71	90.27	9.43				
21. Philip V. n.c. 200	"	8.59	85.15	11.12		2.85	0.42	
22. Athenian (?)	"	8.61	88.34	9.95		0.63	0.26	
23. Ptolemy IX. n.c. 70	"	8.81	84.25	15.64			trace	
24. Pompey, n.c. 53	"	8.70	74.17	8.47		16.15	0.28	
25. Attilia family, n.c. 45	"	9.02	68.69	4.86		25.43	0.11	
26. Julius and Augustus, n.c. 42	"	8.64	79.13	8.00		12.80	trace	
27. Augustus and Agrippa n.c. 30	"	8.65	78.45	12.96		8.62	trace	
28. St. Samosata	"	8.53	70.91	6.75		21.96	"	
29. Victorinus, Sen.	"	8.77	95.37	0.99		trace	"	Silver 1.60
30. "	"	8.73	97.13	0.10		"	1.01	1.76
31. Tetricus, Sen.	"	98.50	0.37			"	0.46	0.76
32. "	"	98.00	0.50			"	0.05	1.15
33. Claudius Gothicus	"	8.81	81.60	7.41		8.11		1.86
34. "	"	8.71	84.70	3.01	trace	2.67	0.31	7.93
35. Tacitus	"	8.72	86.08	3.63		4.87		4.40
36. "	"	8.70	91.46				2.31	5.92
37. Probus	"	8.72	90.68	2.00	1.39	2.33	0.61	2.24
38. "	"	8.74	94.65	0.45		0.44	0.80	3.22
39. Broken sword-blade	"	85.62	10.02				0.44	
40. Fragment of sword-blade	"	91.79	8.17				trace	
41. Broken spear-head	"	99.71						Sulphur 0.28
42. Celt (Ireland)	"	90.68	7.43			1.28	trace	
43. "	"	90.18	9.81					
44. "	"	89.33	9.19				0.33	0.24
45. "	"	83.61	10.79			3.20	0.58	Cobalt 0.34
46. Celtic weapon*	Fresenius	92.00	6.70			0.69	0.29	Nickel 0.31

\* J. pr. Chem. xl. 374.

<sup>b</sup> Chem. Soc. Qu. J. iv. 252.<sup>c</sup> Otto Lerch, d. anorg. Chem. 3 Aufl. II. [2] 256.

TABLE B. (continued).

	Authority.	Copper.	Tin.	Zinc.	Lead.	Iron.	
47. Celtic vessels . . .	Clarke . .	88.00	12.00				
48. Coffin from the Altai . .	" . .	80.27	19.66				
49. " " . . .	Göbel . .	73.00	26.74				
50. Egyptian dagger . . .	Vauquelin .	85.00	14.00				
51. Gallo-Roman axe . . .	Girardin .	77.77	19.61	1.44	1.18		
52. Axe . . .	" . .	74.9	25.10				
53. Small statue found in . .	Erdmann .	92.58	6.33			0.99	
54. " " the Olden- . .	" . .	85.41	12.13		1.09	0.61	
55. Weapon } burg dis- . .	" . .	91.90	6.84			0.44	
56. " } trict. <sup>4</sup> . .	" . .	90.56	8.23			0.28	
57. Gallic bell* . . .	Girardin .	85.90	14.10				
58. Etruscan vessel . . .	" . .	85.00	14.20	0.80			
59. Mirror . . .	" . .	78.50	21.50				
60. Buckle . . .	" . .	37.20	18.80		44.00	trace	Antimony trace
61. Ring . . .	" . .	45.10	14.00		40.90		
62. Girdle-buckle . . .	" . .	69.30	20.80		9.90		
63. Buckle . . .	" . .	72.00			28.00		
64. Bells of the 12th century .	" . .	76.10	22.30	1.60	trace	1.60	
65. " " . . .	" . .	71.00	26.00	1.80		1.20	
66. Hooks of the 14th century .	" . .	71.90	6.10		27.90		
67. Celtic weapon . . .	Donovan .	85.23	13.11		1.14		Carbon Sulphur
68. Drinking horn . . .	" . .	79.34	10.87		9.11		
69. Bronze ring . . .	Salvetat .	75.55	23.52		0.47		
70. " " . . .	" . .	79.93	15.53		3.50		
71. Column in the Place Vendôme <sup>f</sup> . .	D'Arcet .	89.16	10.24	0.49	0.10		
72. Axle-tree bed of — English locomotive* . .	E. Schmid .	73.60	9.50	9.00	7.0	0.42	
73. Belgian " . . .	" . .	89.00	2.50	7.80		0.80	
74. Seraing " . . .	" . .	86.00	14.00				
75. Stuffing-box, Belgian . .	" . .	90.20	3.50	6.40			
76. Piston of Locomotive, Seraing . . .	" . .	89.00	2.40	9.00			
77. Regulator, Belgian locomotive . . .	" . .	86.80	12.40				
78. Stephenson's journals . .	" . .	79.00	8.0	5.80	8.00		
79. Fenton's " . . .	" . .	5.50	14.5	80.00			
80. Deurance's " . . .	" . .	22.22	33.33				Antimony 44.44
81. Frictional bearings . . .	" . .	80.00	16.00				2.00
82. Concussion " . . .	" . .	74.00	3.70	22.22			
83. Bearings in hot situations .	" . .	85.00	2.50	5.00	1.25		
84. Small machine-wheel . .	Köchlin .	90.00	10.00				
85. Die for gold-working . . .	" . .	83.33	16.66				Bismuth 0.5
86. White table-gong . . .	" . .	17.00	80.00				
87. Chinese gong <sup>h</sup> . . .	Thomson .	80.5	19.5				
88. Tam-tams <sup>i</sup> . . .	Klaproth .	78.00	22.00				
89. Speculum <sup>k</sup> . . .	Otto . .	65.15	32.78				
90. French coin . . .	König . .	95.00	4.00	1.00		0.56	
91. Old bell at Rouen <sup>l</sup> . . .	Girardin .	71.0	26.0	1.8		1.2	

<sup>d</sup> J. pr. Chem. lxxi. 231.<sup>e</sup> J. pr. Chem. lx. 91.<sup>f</sup> Otto Lehrs, d. anorg. Chemie, 3 Aufl. ii. [3] 255.<sup>g</sup> Jahrb. d. Chem. 1850. p. 637.<sup>h</sup> Ann. Phil. ii. 209.<sup>i</sup> Handw. d. Chem. 2 Aufl. ii. [3] 302.<sup>k</sup> Ann. Ch. Pharm. cli. 65.<sup>l</sup> Ann. Ch. Phys. [2] i. 305.



19. With **Zinc** (Gm. v. 477).—The most important alloy of these metals is *brass*, which contains about 2 pts. by weight of copper to 1 pt. of zinc. Other proportions form *Tombac*, *Pinchbeck*, *Prince's metal*, *Similor*, *Mannheim gold*, *Mosaic gold*, &c.

The alloys are prepared: 1. By adding zinc to melted copper, or by fusing the metals together in a covered crucible, the zinc being placed below, and the copper in small pieces at top. For brass, the proportion is 7 pts. copper to 3 pts. zinc. Part of the zinc always burns away. The fusion is performed in crucibles, seven of which are usually placed in a circular air-furnace.—2. By igniting copper in small pieces with zinc-oxide and charcoal or coal powder. In this older method of making brass, roasted native calamine or furnace-calamine is ignited in covered crucibles with charcoal powder and copper, the latter being cut into small pieces or granulated.—3. Copper exposed at a red heat to vapours of zinc is completely penetrated by them, but does not lose its form.—*Lyons Gold-lace* is prepared by exposing rods of copper to the vapour of zinc till they are converted into brass on the surface, and then drawing them out into wire. A copper coin placed in a crucible above a mixture of zinc-oxide and charcoal, and moderately ignited, is converted into brass without obliteration of the device.—4. By precipitation. *Spurious gold-wire* is prepared by boiling copper-wire (previously cleaned with nitric acid) with hydrochloric acid, cream of tartar, and a mixture of 1 pt. zinc and 12 pts. mercury. When sulphate of copper dissolved in 20 pts. water, is precipitated by zinc, the black flakes at first thrown down are an alloy of copper and zinc.

Copper alloyed with a small quantity of zinc exhibits a paler red and yellowish-red colour; a larger quantity renders it yellow, the colour being brightest when the two metals are united in equal parts; a still greater quantity of zinc makes it white (Lewis). In certain proportions, the alloy of copper and zinc is more ductile at ordinary temperatures than pure copper, but generally brittle at a red heat. Very small quantities of zinc do not impair the ductility of copper at ordinary temperatures, excepting that, when thus alloyed, it sooner becomes hard and brittle by hammering, and therefore requires to be oftener heated to redness; but even 0.6 per cent. of zinc is sufficient to cause copper to crack when hammered at a red heat (Karsten). The most ductile of all the alloys of copper and zinc are those which contain 84.5 per cent. of copper to 15.5 of zinc (tombac), and 71.5 copper to 28.5 zinc (brass). The alloy formed of equal weights of the two metals cracks in rolling. An excess of zinc renders the alloy brittle, the most brittle of all being that which contains 1 at. copper to  $1\frac{1}{2}$  to 2 at. zinc (Karsten.) Small quantities of lead diminish the ductility of the alloy; tin increases its hardness. (Karsten.)

All alloys in which the amount of zinc does not exceed 50 per cent. exhibit the reaction of copper towards acids and in the voltaic circuit, and they do not precipitate the salts of copper. But alloys containing excess of zinc decompose copper-salts, being thereby converted into perfectly pure copper; they likewise dissolve completely in acids which have no action on copper alone, the solution taking place the more quickly as the excess of zinc is greater. If the quantity of acid is insufficient to dissolve the whole, the copper first dissolved is reprecipitated, the liquid at length retaining nothing but zinc (Karsten). Brass turns red when rubbed with hydrochloric acid, because the acid dissolves the zinc in preference to the copper; but when rubbed with ammonia, it turns white, because the ammonia dissolves out the copper. (Berzelius.)

TABLE C.—*Properties of Alloys of Copper and Zinc*, according to Mallet (Dingl. polyt. J. lxxxv. 378).

At.* Cu. Zn.	Per cent. Cu.	Specific gravity.	Colour.	Fracture.	Tenacity.	Order of Mallea- bility.	Order of Hard- ness.	Order of Fusi- bility.
1 : 0	100	8.667	r.	.	24.6	8	22	15
10 : 1	90.72	8.605	r. y.	c. gr.	12.1	6	21	14
9 : 1	98.80	8.607	r. y.	f. gr.	11.5	4	20	13
8 : 1	88.60	8.633	r. y.	f. gr.	12.8	2	19	12
7 : 1	87.30	8.587	r. y.	f. gr.	13.2	0	18	11
6 : 1	85.40	8.591	y. r.	f. f.	11.1	5	17	10
5 : 1	83.02	8.415	y. r.	f. f.	13.7	11	16	9
4 : 1	79.65	8.448	y. r.	f. f.	14.7	7	15	8
3 : 1	74.58	8.397	pale y.	f. f.	13.1	10	14	7
2 : 1	66.18	8.299	deep y.	f. f.	12.5	3	23	6
1 : 1	49.47	8.230	deep y.	c. g.	9.2	12	12	6
1 : 2	32.85	8.263	dark y.	c. gr.	19.3	1	10	6

\* See Note p. 43.

TABLE C. (continued).

At. Cu. Zn.	Per cent. Cu.	Specific gravity.	Colour.	Fracture.	Tenacity.	Order of Mallea- bility.	Order of Hard- ness.	Order of Fusi- bility.
8 : 17	31.52	7.721	silv. w.	c.	2.1	v. br.	5	5
8 : 18	30.36	7.836	silv. w.	v. c.	2.2	v. br.	6	5
8 : 19	29.17	7.019	light gr.	c.	0.7	v. br.	7	5
8 : 20	28.12	7.603	ash-gr.	v.	3.2	br.	3	5
8 : 21	27.10	8.058	light gr.	c.	0.9	br.	9	5
8 : 22	26.24	7.882	light gr.	c.	0.8	v. br.	8	5
8 : 23	25.39	7.443	ash-gr.	f. gr.	5.9	s. d.	1	5
1 : 3	24.50	7.449	ash-gr.	f. gr.	3.1	v. br.	2	4
1 : 4	19.65	7.371	ash-gr.	f. gr.	1.9	br.	4	3
1 : 5	16.36	6.605	dark gr.	f. gr.	1.8	br.	11	2
0 : 1	0	6.895	.	.	15.2	.	23	1

In this table, *r* under *Colour*, denotes red, *y.* yellow, *gr.* grey, *silv. w.* silver-white. Under *Fracture*, *c. gr.* denotes coarse-grained, *f. gr.* fine-grained, *f. f.* fine-fibred, *c.* conchoidal, *v.* vitreous, *lam.* laminar. The numbers under *Tenacity* denote the weight in tons required to break a rod whose transverse section measures a square inch. Under *Malleability*, *br.* signifies brittle, *v. br.* very brittle, *s. d.* slightly ductile: the malleability was determined at 60° F. (15.6 C.). Under *Hardness* and *Fusibility*, the number 1 denotes the minimum.

The compound corresponding in percentage composition to  $\text{ZnCu}^3$  is *Prince's metal*, or *Bath metal*;  $\text{ZnCu}^4$  is German and Dutch brass;  $\text{ZnCu}^5$  is rolled brass;  $\text{ZnCu}^2$  is English brass;  $\text{ZnCu}$  is German brass;  $\text{Zn}^2\text{Cu}$  is German brass for watchmakers, (Mallet.)

From experiments by F. H. Storer (*Memoirs of the American Academy*, New Series, viii. 97), it appears that alloys of copper and zinc, formed by melting the two metals together in the most varied proportions, then leaving the mass to cool partially, and pouring out the still fluid portion (as for the crystallisation of bismuth, i. 590), yield crystals of similar aspect, sometimes exhibiting distinct octahedral faces, sometimes in confused aggregates of crystals, but all of octahedral character, and bearing a striking resemblance to the crystals of pure copper obtained by fusion. From this resemblance, and from the observations of Nicklès (*Jahresber. d. Chem.* 1847—8, p. 434), that zinc crystallises in forms belonging to the regular system, Storer concludes that all the alloys of copper and zinc also crystallise in that system, and are not definite atomic compounds, but merely isomorphous mixtures of the two metals,—a conclusion further supported by the fact that none of the crystals were found to contain a larger proportion of either metal than the remainder of the molten liquid from which they had separated. The alloy containing from 5 to 6 per cent. of zinc was found to crystallise particularly well; the white alloys are difficult to crystallise, having a great tendency to assume the pasty condition on cooling. Alloys containing from 58 to 43 per cent. copper are much inclined, especially when quickly cooled, to form fibrous aggregates of crystals. The colours of the different alloys (on recently filed surfaces) exhibit a perfectly regular transition, without any sudden leaps, from the pure red of copper to yellow, and ultimately to white. The purest yellow is exhibited by those containing from 75 to 80 per cent. copper. The hardness increases with the proportion of zinc. Sudden cooling in water renders the alloys, for the most part, softer and less tenacious.

**Brass**.—This alloy is harder than copper, and therefore resists wear better. It is very malleable and ductile, and may be raised by stamping into various objects, such as curtain-bands. At a red heat, however, it is very brittle. It is well adapted for casting, being easily fusible, and capable of receiving very delicate impressions from the mould. It is said to resist atmospheric influences better than copper; but when its surface is unprotected by lacquer, it rapidly tarnishes and becomes black.

During the process of stamping brass, that is, of subjecting it to heavy blows in dies, as for the manufacture of curtain-bands, &c., the metal requires to be annealed from time to time, and at the completion of the process the article remains discoloured by adhering oxide. This is removed by "dipping" the metal in aqua fortis of suitable strength, and then washing it with water. A bright metallic surface is thus produced, ready to receive the lacquer (a solution of shellac in alcohol). The colour may be varied by using acid of different strengths.

The pale yellow dead surface often seen on ornamental articles is produced by



"pickling" the metal, after stamping, in weak aqua fortis (say 1 pt. strong nitric acid to 7 or 8 pts. water); then, after washing with water, immersing it in much stronger acid, till a white "curd," due to a stratum of small gas bubbles, forms on the surface; again washing with water; roughly drying the object by moving it about in cold sawdust; then dipping it again in strong nitric acid for a few seconds; washing first in water, then in a cold solution of argol or impure cream of tartar; and lastly drying in hot sawdust.

The surface of brass is often coloured or bronzed after "dipping" and before lacquering. This is done by immersing the article in a solution of arsenious acid in hydrochloric acid, by applying a dilute aqueous solution of chloride of platinum, or an aqueous solution of corrosive sublimate mixed with vinegar, or by rubbing plumbago over the surface. Either of these applications produces a dark grey coating, which assumes a bronze-tint when lacquered. The corrosive sublimate solution is used for common work; the platinum-process for theodolites, levels, and other instruments. (*Percy's Metallurgy*.)

*Muntz's metal.*—This alloy and its application "for sheathing the bottoms of ships, and other such vessels," was the subject of a patent granted to the late G. F. Muntz of Birmingham, in 1832. The proportions specially recommended in the specification are 60 per cent. copper and 40 zinc; but these proportions may be varied from 50 up to 63 per cent., and from 50 down to 37 per cent. zinc. The metal is cast into ingots, and rolled while hot into sheets, which, when finished, are "pickled" in dilute sulphuric acid, and afterwards washed in water. In the same year Mr. Muntz obtained a second patent for "an improved manufacture of bolts, and other the like for ships' fastenings," the same proportions of copper and zinc being used; and in 1846, a third patent for the use of an alloy consisting of 56 per cent. copper, 43½ zinc, and 3½ lead. This last alloy does not appear to have been manufactured on a large scale, but Dr. Percy states that he has succeeded in rolling brass well, which contained not less than 8 per cent. of lead.

Muntz's metal, or yellow-metal sheathing, has entirely superseded copper sheathing in the merchant service, though the latter is still retained in the navy. Its special advantages are said to be that it keeps the bottoms of ships cleaner and costs much less than copper sheathing. It is now generally made in reverberatory furnaces, the zinc being cautiously added to the melted copper, and the melted metal tapped into a vessel lined with clay, out of which it is ladled into suitable cast iron ingot-moulds.

*Mosaic gold.*—Prepared by fusing equal weights of copper and zinc in a crucible at the lowest possible temperature, stirring constantly, and then adding a further quantity of zinc in small portions, till the colour of the fused mixture, after passing through the various shades of brass-yellow, purple-red, and violet, has become perfectly white. The alloy, after casting in the mould and cooling, exhibits the colour of gold, and does not tarnish by exposure to the air, even in the neighbourhood of the sea. (Hamilton and Parker, Edinb. J. of Sc. 1826.)

*Brass solder.*—2 pts. brass to 1 zinc, or if it is to be more ductile, 6 pts. brass, 5 silver, and 2 zinc.

*Imitation bronze, Tombac, Pinchbeck, Prince's metal, Similor, Mannheim gold.*—These terms are applied to alloys of zinc and copper, containing 80 per cent. or more of copper; also to alloys of copper with zinc, tin, and lead. The cheapness of zinc compared with tin, has caused these alloys to be extensively used of late years as substitutes for true bronze, which is an alloy of copper and tin, especially for ornamental articles, which are gilt or artificially bronzed on the surface. Alloys whose composition ranges from 85·5 per cent. copper, 11·5 zinc, and 4 tin, to 66 copper, 32 zinc, and 2 tin, may likewise be used for the casting of statues, as they run well into the mould, and are easily filed and chiselled. Those which approach to the latter composition, 66 per cent. copper, &c., are too yellow to be used, excepting for objects which are to be gilt or artificially bronzed; but the first-mentioned alloy yields a cast of a fine deep red colour, which, by exposure to the air, slowly acquires a very beautiful tarnish.

The alloy called *tombac*, containing 84·5 per cent. copper and 15·5 zinc, is very ductile and malleable. *Dutch-metal* is tombac beaten out into leaves  $\frac{1}{32000}$  of an inch thick.

*Bronze-colours or Bronze-powders*, used for colouring objects cast in brass, imitation bronze, or plaster of Paris, and for various other ornamental purposes, are prepared by triturating Dutch-metal or other alloys of copper and zinc, &c., between rollers with water and resin, oil or fat, separating the finer particles from the grosser by levigation, sifting, &c., and lastly drying and heating them. (See *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 463.)

The following Table exhibits the composition of various kinds of brass and imitation-bronze. See also Nos. 72, 73, 75, 76, 78, 79, and 82 of Table B, p. 46.



TABLE D.—Composition of various Alloys of Copper and Zinc used in the Arts.

	Authority.	Copper.	Zinc.	Tin.	Lead.	Iron.
1. Brass, English . . . .	Lavater <sup>a</sup>	70.29	29.26	0.17	0.28	
2. Brass from Heegermahl . . . .	"	70.16	27.45	0.79	0.20	
3. " Angsburg . . . .	"	71.89	27.63	0.85		
4. " Neustadt, Eberswald . . . .	Kadernatsch <sup>b</sup>	71.36	28.15			
5. " Romilly . . . .	Chaudet <sup>c</sup>	70.1	29.9			
6. " of unknown origin . . . .	Karsten <sup>d</sup>	71.5	28.5			
7. " " " " " " " " " "	Regnault <sup>e</sup>	71.0	27.6	trace	1.3	
8. " " " " " " " " " "	Chaudet <sup>d</sup>	61.59	35.33	0.25	2.86	
9. " Stolberg . . . .	"	65.80	31.80	0.25	2.15	
10. Watch-wheels . . . .	Faist <sup>f</sup>	60.66	36.88	1.35		0.74
11. " " " " " " " " " "	"	66.06	31.46	1.43		0.88
12. Ship-nails, bad . . . .	Percy <sup>g</sup>	52.73	41.18		4.72	
13. " good . . . .	"	62.62	24.64	2.64	8.69	
14. Tombac, English . . . .	Faist <sup>f</sup>	86.38	13.61			trace
15. " German . . . .	Karsten <sup>h</sup>	84.0	15.5			
16. Coin of Titus Claudius . . . .	Girardin <sup>i</sup>	81.4	18.6			
17. " Cassia family, B. C. 20 (sp. gr. 8.59) . . . .	Phillips <sup>k</sup>	82.26	17.31			0.35
18. " Nero, A. D. 60 (sp. gr. 8.50) . . . .	"	81.07	17.81	1.05		
19. " Titus, A. D. 79 (sp. gr. 8.30) . . . .	"	83.04	15.84			0.50
20. " Hadrian, A. D. 120 (sp. gr. 8.33) . . . .	"	85.67	10.83	1.14	1.73	0.74
21. " Faustina, jun., A. D. 165 . . . .	"	79.15	6.7	4.97	9.18	0.23
22. Antique bracelet, Naumburg . . . .	Göbel <sup>l</sup>	83.08	15.38	1.64		
23. " fibula, Königsberg . . . .	"	82.5	16	1.5		
24. " chain, Ronneburg . . . .	"	82.5	17.5			
25. Statue of Louis XIV. (sp. gr. 8.482) . . . .	D'Arcet <sup>m</sup>	91.45	5.53	1.70	1.37	
26. " Henri IV. . . .	"	89.62	5.70	4.20	0.48	
27. " Louis XV. . . .	"	82.45	10.30	4.10		
28. " Minerva in Paris . . . .	"	83.00	14.00	2.00	1.00	
29. " Napoleon . . . .	"	75.00	20.00	3.00	2.00	
30. " Lessing, in Brunswick . . . .	Otto <sup>n</sup>	84.20	11.50	3.55	0.75	
31. Bronze for gilding . . . .	D'Arcet <sup>m</sup>	82.00	18.00	2.50		
32. " " " " " " " " " "	"	64.50	32.50	0.25		
33. " " " " " " " " " "	"	82.00	18.00	3.00		
34. " " " " " " " " " "	"	78.00	18.00	2.00		
35. Bronze-colour, pale yellow . . . .	König <sup>o</sup>	82.33	16.69			
36. " deep yellow . . . .	"	84.50	15.30			0.16
37. " red-yellow . . . .	"	90.00	9.60			0.07
38. " orange . . . .	"	98.93	0.73			0.20
39. " copper-red . . . .	"	99.90				0.08
40. " violet . . . .	"	98.22	0.50	trace		trace
41. " green . . . .	"	84.32	15.02			0.30
42. " white . . . .	"		2.39	96.46		0.03

<sup>a</sup> J. pr. Chem. iii. 198.<sup>b</sup> Pogg. Ann. xxxv. 575.<sup>c</sup> Ann. Ch. Phys. [2] v. 321.<sup>d</sup> Gm. Handb. v. 480.<sup>e</sup> Ibid.<sup>f</sup> Polyt. Centralbl., 1853, p. 571.<sup>g</sup> Jahresb. d. Chem., 1850, p. 637.<sup>h</sup> Gm. Handb. v. 479.<sup>i</sup> Handw. d. Chem. 2 Aufl. ii. [2] 500.<sup>k</sup> Chem. Soc. Qu. J. iv. 252.<sup>l</sup> Schw. J. ix. 407.<sup>m</sup> Handw. loc. cit.<sup>n</sup> Ibid.

*Alloys of Copper, Zinc, and Iron.*—80 pts. zinc, 1 pt. copper, and 1 pt. cast iron form Sorel's *white brass*. It has the aspect and fracture of ordinary zinc, is said to be as hard as copper, and tougher than cast iron, to admit of turning, filing, and boring, and not to rust even in damp situations. (Berthier, Pogg. Ann. lxx. 344.)

*Alloys of Copper, Zinc and Nickel.*—*Nickel-silver, German-silver, White copper, Packtong or Packfong, Weisskupfer, Neu-silber, Argentan, Maillechort.*—To prepare this alloy, which is much used as a substitute for silver, the copper and nickel are first melted in a crucible, and the zinc is then added in pieces previously heated. Or, the three metals, in a state of fine division, are mixed together in a crucible, copper being placed at top and bottom, the whole covered with charcoal powder and heated in an air-furnace with a strong draught, the mixture being stirred all the while, to ensure the complete solution of the difficultly fusible nickel. The longer and the more completely the mixture is fused, the more ductile does it become; part of the zinc burns away. (Gersdorff, Pogg. Ann. viii. 103.)

*Proportions of the materials.*—*a.* 2 pts. copper, 1 nickel, 1 zinc: serves for spoons and forks. *b.* 5 pts. copper, 2 nickel, 2 zinc: has the colour of silver alloyed with  $\frac{1}{2}$  pt. copper; serves for knife and fork handles, snuffers, &c. *c.* 3 pts. copper, 1 nickel, 1 zinc: this proportion gives the best alloy for rolling. The addition of 3 pts. of lead to 100 pts. of the mixture *a*, or of 2 pts. lead to 100 pts. of the mixture *b*, yields an alloy adapted for cast articles, such as candlesticks, spurs, and bells. The addition of 2.5 pts. of iron or steel to 100 pts. of alloy, renders it much whiter, but likewise harder and more brittle; the iron must be previously fused with a portion of the copper, under a layer of charcoal-powder in the blast-furnace, and then melted together with the zinc and nickel and the rest of the copper (Gersdorff). *d.* 8 pts. copper, 3 nickel, and 5 zinc yield very good nickel-silver (Frick). An alloy of 10 pts. copper, 1 nickel, and 5 zinc, has still a pale yellow colour; that which contains 10 copper, 1 nickel and 7 zinc, is yellowish-white and less ductile than *d* (Frick). Larger quantities of iron do not enter into combination with the nickel-silver as a whole, but unite with part of the copper, nickel, and carbon, forming an alloy which floats like drops of oil on the surface of the nickel-silver. (Erdmann.)

Nickel-silver has a crystalline structure when solidified from fusion. It must, therefore, be heated to dull redness and cooled again completely before it is rolled or hammered; when once the crystalline structure has been destroyed, the alloy may be worked like brass (Gersdorff). Chinese nickel-silver may be worked even at a dull red heat, but at a stronger heat it flies to pieces on the slightest stroke of the hammer (Fyfe, Edinb. Phil. J. vii. 69). Nickel-silver is harder than silver, and susceptible of a high polish. Its colour approaches that of silver, but is greyer. A mixture of 1 pt. oil of vitriol and 7 pts. water turns it white when boiled with it (Gersdorff). It is not magnetic, or but slightly so; when it contains a certain amount of iron. It fuses at a bright red heat, the zinc burning away if the air has access to it. When exposed to the air, it acquires a slight yellow tarnish. When immersed in vinegar, it becomes coated with verdigris, only at those parts where the air can likewise act upon it (Frick). In vinegar it becomes greenish black; in wine, dark brown; in solution of common salt, red brown; in solution of sal-ammoniac or tartaric acid, black with green spots; and in oxalic acid, black (D'Arcet, J. Pharm. xxiii. 223). In water containing  $\frac{350}{1000}$  of potash-hydrate, it remains bright. (A. Vogel.)

*Analyses of Commercial Nickel-silver.*

	Fyfe.	Smith.	O. Henry.	D'Arcet.		Lonyet.			Elsner.
	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>	<i>e.</i>	<i>f.</i>	<i>g.</i>	<i>h.</i>	<i>i.</i>
Zn	25.4	17.8	13.6	31.25	17	17.01	22.15	26.05	25.0
Sn	.	.	.	.	2				
Fe	2.6	.	trace	.	3	trace	trace	trace	3.0
Co	.	3.4							
Ni	31.6	18.8	19.3	18.75	23	19.13	15.05	10.85	13.0
Cu	40.4	60.0	66.0	50.00	55	63.34	62.40	62.63	57.4
	100.0	100.0	98.9	100.00	100	99.48	99.60	99.53	98.4

*a.* Chinese packfong, of specific gravity 8.432. *b.* English nickel-silver, somewhat yellower than the German. *c.* Parisian Maillechort; contains also a trace of arsenic, which remains behind when the alloy is dissolved in nitric acid. *d* and *e.* From unknown sources. *f, g, and h.* English nickel-silver, used in Birmingham for articles that are to be plated. *i.* From Sheffield, distinguished by extraordinary elasticity, used for the friskets of printing-presses.

*American nickel-silver.*—1 pt. iron, 1 cobalt, 2 silver, 2 tin, 4 manganese, 24 nickel, 36 zinc, and 96 copper. (Gm. v. 498.)

**COPPER, BROMIDES OF.** Copper does not unite with bromine at ordinary temperatures, but on the application of heat, combination takes place, the chief product being the hemibromide,  $\text{Cu}^{\text{H}}\text{Br}$ .



*Protobromide of Copper*, or *Cupric Bromide*,  $\text{CuBr}_2$ , is formed by evaporating the solution of cupric oxide in aqueous hydrobromic acid, and fusing the residue at a gentle heat. The residue is iron-black like plumbago. If the solution be left to evaporate in vacuo over oil of vitriol, anhydrous shining crystals are obtained, resembling iodine in appearance (Rammelsberg, Pogg. Ann. lv. 246). According to Berthelot, protobromide of copper gives off half its bromine even below a red heat; according to Rammelsberg, it gives off 36.8 per cent. and leaves cuprous bromide.

*Hydrated Protobromide of copper*, or *Hydrobromate of cupric oxide*.—The emerald-green solution of cupric bromide in water, or of cupric oxide in aqueous hydrobromic acid, or of copper in a mixture of hydrobromic and nitric acids, becomes brown on evaporation, and yields right rectangular prisms (greenish-yellow needles, according to Berthelot), which fuse at a gentle heat, giving off their water and leaving a residue of anhydrous protobromide of copper.

Protobromide of copper and the hydrated crystals deliquesce in the air, and dissolve readily in water; the green solution turns brown on evaporation, and likewise when mixed with oil of vitriol or with salts, these substances depriving it of its water (Löwig). Ammonia added to the solution in quantity not sufficient for complete precipitation, forms a pale green precipitate of hydrated oxybromide.

*Ammonio-cupric bromides*.—The compound  $2\text{CuBr} \cdot 5\text{NH}_3$ , is obtained by the action of dry ammonia gas on cupric bromide. It is a bluish powder, which, when heated, gives off water and bromide of ammonium. It dissolves in a small quantity of water, forming a deep blue solution, which becomes turbid when diluted, depositing hydrated cupric oxide, which turns black when heated in the liquid (Rammelsberg, loc. cit.). Another ammonio-bromide, containing  $2\text{CuBr} \cdot 3\text{NH}_3$ , is obtained by mixing a strong solution of cupric bromide with a sufficient quantity of strong ammonia to form a clear solution, and then adding alcohol. It forms small dark-green crystals, but in other respects resembles the preceding. Rammelsberg found in the former of these compounds 28.98 per cent., in the latter 19.98 per cent. ammonia.

*Hemibromide of Copper*, or *Cuprous Bromide*,  $\text{Cu}^+\text{Br}$ , or  $\text{CuBr}$ . *Dibromide of copper*.—When bromine is poured into the sealed end of a glass tube, the upper part of the tube filled with fine copper wire, and the copper heated to dull redness, combination takes place, attended with vivid incandescence. The protobromide which mixes with the mass is dissolved out by water. On dissolving the product in aqueous hydrobromic acid, any copper that may remain uncombined is left behind, and the cuprous bromide may be precipitated from the solution by water (Löwig). Another mode of preparation is to heat thin rolled-up copper-foil in a flask, at the bottom of which some bromine is placed, and when combination attended with ignition is set up, to drop more bromine in, till the whole of the copper disappears. Cuprous bromide is likewise obtained by heating cupric bromide to redness. It is a dark-greenish brown mass, which is decomposed by ignition, in contact with the air, is insoluble in water, but dissolves without colour in hydrobromic or hydrochloric acid. Nitric acid decomposes it, with evolution of nitric oxide. It is not acted on by sulphuric or acetic acid, even at the boiling heat. It is said to dissolve in aqueous ammonia, and to yield by evaporation crystals of an ammonio-bromide. (Berthelot.)

**COPPER, CARBIDE OR CARBURET OF.** Copper does not appear to form any definite compound with carbon. Pure (electrotype) copper may be fused under charcoal powder without undergoing any change of physical properties. Ordinary copper thus treated becomes brittle at a red heat; but the change is probably due to the presence of small quantities of foreign metals, as in overpoled copper (p. 29). Whether any small quantity of carbon is taken up by the copper has not been exactly ascertained. (Percy's Metallurgy, i. 269.)

**COPPER, CHLORIDES OF.** *a. Protochloride of Copper, Cupric Chloride, Chloride of Cupricum.*  $\text{CuCl}_2$ .—This compound is obtained in the anhydrous state: 1. By the combustion of copper in chlorine-gas. Copper filings or copper foil introduced into dry chlorine, takes fire spontaneously, and burns with a greenish light, producing a mixture of cupric and cuprous chlorides, and if the chlorine is in excess, the latter is slowly converted into cupric chloride.—2. By heating the hydrated chloride to  $200^\circ \text{C}$ .

Anhydrous cupric chloride prepared by (1) forms a brown sublimate; by (2), a brownish-yellow powder. It has a caustic metallic taste, is fusible, and at a red heat gives off half its chlorine, and is converted into the hemichloride. Heated in a current of *phosphoretted hydrogen*, it yields hydrochloric acid gas and triphosphide of copper. Fused with *phosphorus*, it forms chloride of phosphorus and phosphide of copper (H. Rose, Pogg. Ann. xxvii. 117). It is not decomposed by *sulphuric anhydride* at ordinary temperatures (H. Rose, *ibid.* xxxviii. 121). *Sulphuric acid* does not decompose it at ordinary temperatures, but completely when heated, hydrochloric



acid being evolved (A. Vogel). Heated in a current of *ethylene gas*, protochloride of copper yields a mixture of copper and cuprous chloride (Wöhler). When exposed to the air, it turns green and deliquesces.

*Hydrated protochloride of copper* is produced: 1. By the deliquescence of the anhydrous chloride.—2. When copper immersed in hydrochloric acid is exposed to the air for a considerable time.—3. By dissolving copper in aqua regia.—4. By dissolving cupric oxide or carbonate in hydrochloric acid. The solution of cupric oxide in concentrated hydrochloric acid is attended with great development of heat.—5. By pouring a small quantity of water at  $50^{\circ}$ – $60^{\circ}$  C. on a mixture of equal weights of pulverised sulphate of copper and common salt. The dark green liquid thus formed deposits, on cooling, crystals of sulphate of sodium, and by further evaporation the remainder of this salt, together with the excess of chloride of sodium: the decanted solution finally yields crystals of cupric chloride (Rieckher.) The emerald-green solution evaporated and cooled, yields green right-angled four-sided prisms, which at  $100^{\circ}$  C. turn brown, giving off the greater part of their water, but do not part with the whole, which amounts to 21.53 per cent., till they are heated to  $200^{\circ}$  (Graham, Ann. Ch. Pharm. xxix. 31). Cold sulphuric acid likewise abstracts water from them, and converts them into the brown anhydrous protochloride, which it does not dissolve or decompose (A. Vogel). The crystals deliquesce in the air.

From the aqueous solution, *phosphorus* throws down hemichloride of copper, and forms phosphoric acid (Boeck); the same precipitate is likewise produced by *mercury*, with formation of mercurous chloride; by *silver*, with formation of chloride of silver, black at first, but afterwards white (Wetzlar, Schw. J. lii. 475); and by *di-chloride of tin*, with formation of tetrachloride of tin. Cuprous chloride is also precipitated on boiling the aqueous solution with *sugar*, and partly remains dissolved in the hydrochloric acid produced by the reaction (A. Vogel); a solution of protochloride of copper mixed with *ether*, and exposed to the sun's rays, loses its colour, and on the addition of water yields a precipitate of cuprous chloride. (Gehlen.)

The solution of protochloride of copper in a small quantity of water is emerald-green, but a larger quantity turns it pale blue. The concentrated solution assumes a yellow colour on the addition of strong hydrochloric acid. With strong sulphuric acid, it solidifies to a brown mass. Characters traced on paper with the solution turn yellow when heated, the writing disappearing as the paper cools.

Protochloride of copper is soluble in *alcohol* and in *ether*.

For the so-called *basic chlorides of copper*, see COPPER, OXYCHLORIDES OF.

*Ammonio-cupric Chlorides*.—100 pts. of dry cupric chloride quickly absorb 73.7 pts. ammonia, crumbling at the same time to a blue powder. The resulting compound,

which has the composition  $3\text{NH}^3\cdot\text{CuCl}$ , or possibly  $\text{NH}\text{Cu}(\text{NH}^3)_2\text{Cl}$ , gives off part of its ammonia on exposure to the air, and turns green. At  $140^{\circ}$  C. it gives off 2 at. ammonia, leaving an apple-green powder consisting of *chloride of cuprammonium*,  $\text{NH}^3\text{Cu}\cdot\text{Cl}$ . At a higher temperature, it gives off sal-ammoniac and a small quantity nitrogen, and leaves cuprous chloride. (H. Rose.)

The compound  $3\text{NH}^3\cdot\text{CuCl}$  is obtained as a hydrate,  $2(3\text{NH}^3\cdot\text{CuCl})\cdot\text{H}^2\text{O}$ , by passing *ammonia-gas* into a solution of cupric chloride, till the precipitate which first forms is redissolved. The liquid becomes heated nearly to the boiling point, and on cooling deposits the compound in dark blue prisms and octahedrons. (Kane.)

The *di-ammonic compound* is obtained, by passing ammonia-gas in excess through a hot saturated solution of cupric chloride, in dark blue hydrated octahedrons, which at  $149^{\circ}$  C. are reduced to  $\text{NH}^3\cdot\text{CuCl}$ .

The *oxychloride*,  $\text{Cu}^2\text{ClO}$ , likewise absorbs ammonia-gas, forming the compound  $\text{NH}^3\cdot\text{Cu}^2\text{ClO}$ .

Protochloride of copper forms double salts with the chlorides of the alkali-metals.

*Chloride of Cupricum and Ammonium* (*Kupfer-salmiak*),  $\text{NH}^4\text{Cl}\cdot\text{CuCl} + \text{H}^2\text{O}$ , is obtained by dissolving 53.4 pts. sal-ammoniac and 67.4 pts. anhydrous or 85.4 pts. crystallised protochloride of copper in a small quantity of water, and leaving the solution to cool. This salt forms bluish-green quadratic octahedrons perfectly soluble in water and alcohol, and easily decomposed by heat (Mitscherlich, Graham); Henmann, by the same mode of preparation, obtained a salt with 2 at. water; so likewise did Hautz, by saturating hydrochloric acid with cupric carbonate, and mixing the solution with half the quantity of hydrochloric acid neutralised with ammonia.

Bequerel obtained several compounds of chloride of ammonium with basic cupric chloride (oxychloride) by filling the bend of a U-tube with clay, placing solution of sal-ammoniac in the one arm, cupric chloride in the other, and immersing the end of a bent strip of copper in each arm in such a manner as not to touch the clay. The end dipping into the sal-ammoniac became covered in the course of a few months with crystals exhibiting remarkable truncations of the angles and edges; they were resolved



by water into chloride of ammonium and oxychloride of copper. A similar compound was obtained with chloride of potassium.

*Chloride of Cupricum and Potassium*,  $\text{KCl.CuCl} + \text{H}_2\text{O}$ , is obtained in the same manner as the corresponding ammonium-salt, according to Mitscherlich, in quadratic octahedrons, according to Jacquelin, in double six-sided pyramids, soluble in water and in alcohol.

**HEMICHLORIDE OF COPPER.** *Cuprous Chloride. Chloride of Cuprosum.*  $\text{Cu}^2\text{Cl}$  or  $\text{CuCl}$ , also called *Dichloride of Copper*, *Boyle's Resina cupri*.—Produced: 1. Together with the protochloride, by the combustion of copper in chlorine gas.—2. Copper heated with protochloride of mercury, yields vapour of mercury and hemichloride of copper (Boyle). The decomposition takes place most readily with 1 pt. copper to 2 pts. corrosive sublimate (J. Davy). More exactly, 64 pts. (2 at.) copper and 136 pts. (1 at.) corrosive sublimate.—3. A plate of copper immersed in hydrochloric acid in a flask containing air, becomes covered with white tetrahedrons of hemichloride of copper (Proust).—4. The compound may also be formed by agitating copper-filings with a solution of the protochloride in a close vessel (Proust).—5. By precipitating cupric sulphate, hydrochlorate, nitrate, or acetate with aqueous dichloride of tin, or by treating cupric hydrate or carbonate with dichloride of tin dissolved in hydrochloric acid (Proust):



6. By treating aqueous protochloride of copper with phosphorus, ether, sugar, &c.—7. By heating the protochloride in a retort for a considerable time; digesting the residue with water for several days with the retort closed, to dissolve out the undecomposed protochloride, and pouring off the resulting solution; the residue consists of hemichloride (Proust).—8. By agitating pulverised cuprous oxide with hydrochloric acid in a close vessel (Proust, Chenevix).

Cuprous chloride, obtained by precipitation, is a white crystalline powder, which acquires a dingy violet and blackish-blue tint by exposure to sunlight. It crystallises from its solution in hot concentrated hydrochloric acid in white tetrahedrons (Proust), which turn bluish when exposed to light. According to J. Davy, it separates in olive-green prisms. It melts somewhat below a red heat, and when slowly cooled, solidifies in a translucent, light yellow mass (greyish-white; Proust); the residue obtained by rapid cooling is of a dark brown colour, and confused texture (J. Davy). Specific gravity of the melted mass = 3.677 (Karsten). In close vessels, it does not volatilise, even when strongly heated; but if heated in the air, it goes off in white vapours.

Heated to redness in a stream of *hydrogen*, it is converted into metal and hydrochloric acid gas; in an atmosphere of *phosphoretted hydrogen*, it yields hexeupric phosphide and hydrochloric acid gas (H. Rose, Pogg. Ann. iv. 110, 205). With *iron-filings* under water, it yields metallic copper and soluble protoxide of iron (Proust). *Ferrous sulphate* added to the solution of the hemichloride in hydrochloric acid, throws down metallic copper (Proust). Hemichloride of copper turns yellow when boiled with *water*; but the decomposition is not complete (Proust). With fused *hydrate of potassium* or the aqueous solution of potash, it yields cuprous oxide and chloride of potassium (Proust). When exposed to the air in the dry state, it slowly attracts moisture and turns green; in the moist state it is quickly converted into a green mass. (Proust). With *nitric acid* it forms first a violet and then a blue solution, the action being attended with great rise of temperature and violent evolution of nitric oxide (Proust). A mixture of hemichloride of copper and *sulphuric acid* assumes a faint violet colour when covered with a thin layer of fuming nitric acid. (Gmelin.)

Hemichloride of copper does not dissolve in water, or in dilute sulphuric acid; but it dissolves without colour in strong hydrochloric acid, in aqueous ammonia, and in solution of common salt. A similar solution is formed by agitating the acid in a close vessel with cuprous oxide, or with a mixture of the protoxide and excess of metallic copper; or by agitating copper-filings with a solution of the protochloride strongly supersaturated with hydrochloric acid; or by mixing the same solution with ether and exposing it to the sun's rays. The colourless liquid prepared hot, deposits crystals of hemichloride of copper on cooling. The solution, when mixed with a considerable quantity of water, deposits the greater part of the hemichloride in the form of a white powder. Small quantities of ammonia added to the solution, produce transparent cubes of hemichloride of copper and ammonium, which dissolve in a larger quantity of ammonia, forming a colourless liquid which turns blue on exposure to the air. Fuming nitric acid imparts to the solution a dark greenish-brown colour, which afterwards changes to yellow with evolution of nitrous gas. (Gmelin.)

The hydrochloric acid solution of hemichloride of copper imparts a blue colour to *molybdic acid*, decolorises recently precipitated *Prussian blue*, throws down calomel from a solution of *corrosive sublimate*, and metallic *gold* from a solution of gold. (Proust.)

*Aqueous cuproso-cupric Chloride* is formed in solution by exposing the solution of cuprous oxide in excess of hydrochloric acid to the air; by mixing the same solution with a solution of protochloride of copper; or by agitating the latter with a small quantity of copper-filings. It is a dark brown liquid. (Proust.)

*Ammonio-cuprous Chloride*.—Hemichloride of copper forms a colourless solution with aqueous ammonia, from which potash throws down cuprous hydrate, provided the ammonia is not in too great excess.

*Chloride of Cuprous and Ammonium*.—The solution of cuprous chloride in strong hydrochloric acid mixed with small quantities of ammonia, deposits transparent crystals which appear to be cubes (Gmelin). A similar compound is likewise formed when a solution of sal-ammoniac in which copper is immersed is exposed to the air. (Becquerel.)

*Chloride of Cuprous and Potassium*,  $2\text{KCl.CuCl}$ , is produced when cuprous chloride, as obtained by mixing its hydrochloric acid solution with water, or by precipitating a cuprous salt with stannous chloride, is boiled with a small quantity of water, and mixed with chloride of potassium as long as the latter continues to dissolve. The solution on cooling deposits cubic crystals. Becquerel, by the electrolytic method described at page 53, obtained tetrahedral crystals of the same or similar constitution; also the corresponding barium-salt.

*Chloride of Cuprous and Sodium*.—Cuprous chloride dissolves very readily in solution of common salt, and on evaporating the liquid in vacuo, the double salt crystallises out; with difficulty, however, on account of its great solubility. Potash throws down cuprous oxide; ferrocyanide of potassium yields a white precipitate.

**COPPER, DETECTION AND ESTIMATION OF.** 1. *Reactions in the Dry Way*.—Copper and its compounds impart a green colour to flame.—The black oxide of copper dissolves by fusion in a vitreous flux, and produces a green glass. Any compound of copper fused with borax in the oxidising flame of the blowpipe forms a transparent glass, which is green while hot, but assumes a beautiful blue colour when cold. In the reducing flame, the glass becomes opaque, and covered on the surface with liver-coloured streaks of cuprous oxide, or metallic copper. This last reaction is somewhat difficult to obtain, especially when the quantity of copper is small, but it may always be ensured by fusing a small piece of metallic tin in the bead. Copper salts mixed with carbonate of sodium or cyanide of potassium, and heated on charcoal before the blowpipe, yield metallic copper. The oxides, carbonates, nitrates, and organic salts of copper are reduced on charcoal without the aid of an alkaline flux.

## 2. Reactions in Solution.

a. *Of Cupric salts*.—These salts in solution have generally a sky-blue colour; a strong solution of the chloride is green, but becomes blue on dilution with water. Copper is separated in the metallic state from its salts by *zinc, iron, lead*, and the more oxidable metals, which are dissolved and take the place of the former metal. Also by *phosphorus* from a solution of the sulphate or nitrate, and from a dilute solution of cupric chloride; but in a strong solution of the latter, phosphorus first produces a white precipitate of cuprous chloride, and then becomes blackened from formation of phosphide of copper. *Wood* precipitates metallic copper from its solutions after long contact. Copper is likewise easily precipitated from its solution by electrolysis, as in the electrolytic process.

*Sulphydric acid* and *alkaline sulphides* throw down a brownish-black precipitate of protosulphide of copper, insoluble in sulphide of potassium or sodium, slightly soluble in sulphide of ammonium.

*Potash* or *soda*, added to the solution of a cupric salt, throws down at first a light blue precipitate of hydrated cupric oxide, which, however, on agitation, takes up a portion of the undecomposed salt, and forms with it a green basic salt. An excess of the alkali throws down the hydrate in bulky blue flakes, which, on boiling the mixture, collect together in the form of a black powder, consisting of the anhydrous oxide. This reaction is greatly modified by the presence of *fixed organic substances*, such as sugar, tartaric acid, &c. In a solution of sulphate of copper, containing such substances in sufficient quantity, potash either produces no precipitate, or one which is quickly redissolved, forming a blue solution; and from this solution, when boiled, the copper is sometimes wholly precipitated as red or yellow cuprous oxide, as when grape-sugar is present, or partially, as with cane-sugar, or not at all, as with tartaric acid.

*Ammonia*, added by degrees, and with constant agitation, to the solution of a cupric salt, first throws down a green basic salt, and afterwards the blue hydrate: an excess of ammonia dissolves the precipitate, forming a deep blue solution. A copper solution diluted so far as to be colourless, becomes distinctly blue on the addition of ammonia.



The blue colour thus produced is still visible, according to Lassaigne, in a solution containing 1 pt. of copper in 100,000 pts. of liquid.

*Carbonate of potassium or sodium* throws down, with evolution of carbonic acid, a greenish-blue precipitate of a basic carbonate of copper, which, on boiling, is converted into the black oxide. *Carbonate of ammonium* produces the same precipitate, but when added in excess, dissolves it abundantly, forming a blue solution.

*Cyanide of potassium* causes a yellowish green precipitate of cupric cyanide, soluble in excess of the reagent: hydrochloric acid throws down white cuprous cyanide from this solution, soluble in excess of acid; sulphydric acid, or sulphide of ammonium, produces no precipitate.

*Ferrocyanide of potassium* forms with cupric salts a deep chocolate-coloured precipitate of ferrocyanide of copper. To very dilute solutions it imparts a reddish colour, which is even more delicate in its indications than the ammonia reaction, being still visible in a solution containing 1 pt. of copper in 400,000 pts. of liquid, according to Lassaigne, and in 1,000,000 pts. according to Sarzeau. Ferrocyanide of copper dissolves in aqueous ammonia, and reappears when the ammonia is evaporated. This reaction serves to detect extremely small quantities of copper, even when associated with other metals. Thus, if a solution containing copper and iron be treated with excess of ammonia, a few drops of ferrocyanide of potassium added, the liquid filtered, and the filtrate left to evaporate in a small white porcelain capsule, ferrocyanide of copper will be left behind, exhibiting its characteristic red colour (Warington, Chem. Soc. Qu. J. v. 137). *Iodide of potassium* added to cupric salts forms a yellow precipitate of cuprous iodide, with separation of iodine. Cupric salts are completely reduced to cuprous salts by *alkaline sulphites*, partially by free sulphurous acid. *Hyposulphites*, at the boiling heat, throw down sulphide of copper.

**B. Of Cuprous salts.**—But few of these salts are capable of existing in solution. Cuprous oxide is decomposed by non-oxidising acids, such as sulphuric, phosphoric, oxalic, acetic, and even by dilute nitric acid, into metallic copper and a cupric salt, and is oxidised by strong nitric acid, yielding cupric nitrate. Hydrochloric acid added in small quantity to cuprous oxide converts it into white cuprous chloride, which dissolves in a larger quantity of the strong acid, forming a solution which is colourless if quite pure, but generally has a brown tint, due to the presence of a small quantity of anhydrous cupric chloride; on exposure to the air, it gradually turns green. The colourless or brownish solution exhibits the following reactions:—

*Water* added in sufficient quantity throws down a white precipitate of cuprous chloride, this compound being soluble only in strong hydrochloric acid.

*Caustic potash*, added in small quantity, neutralises the free acid, and precipitates the white cuprous chloride; in larger quantity it forms a brownish-yellow precipitate of cuprous hydrate, insoluble in excess of potash, soluble in a large quantity of ammonia; when exposed to the air, it gradually turns black.

*Ammonia* in excess forms a colourless solution, which gradually turns blue on exposure. Potash added to this ammoniacal solution throws down the brownish-yellow hydrate, provided the quantity of ammonia present is not very large in proportion to the potash. *Carbonate of ammonium* acts in like manner.

The carbonates, both neutral and acid, of *potassium* and *sodium* form a yellow precipitate of cuprous carbonate.

*Iodide of potassium* forms a white precipitate of cuprous iodide, without liberation of iodine.

*Sulphydric acid* produces a black precipitate of cuprous sulphide. *Alkaline sulphides* produce the same precipitate in solutions previously saturated with ammonia.

*Zinc* and *iron* precipitate metallic copper.

Cuprous solutions are formed by treating the solutions of cupric salts with alkaline sulphites. Free sulphurous acid produces but a partial deoxidation and decoloration, even after prolonged boiling, the product formed being a cuproso-cupric sulphate, which sometimes separates in red crystals; but if potash or ammonia be likewise added, the solution becomes quite colourless even in the cold, and contains a double sulphate of cuprosium and the alkali-metal. This colourless solution behaves with ammonia, and the other reagents above mentioned, in the same manner as the solution of cuprous chloride in hydrochloric acid (excepting that it is not decomposed by dilution), and yields with *cyanide of potassium* a white precipitate of cuprous cyanide, which dissolves in excess of the reagent, forming a solution which is not precipitated by sulphide of ammonium.

Cuprous salts, especially the solution of the chloride in hydrochloric acid, quickly absorb *carbonic oxide gas*. The solution of the chloride saturated with this gas is not precipitated by water, or even by alcohol. (Leblanc.)

*Marsh-gas* is likewise absorbed by the solution of cuprous chloride.



### 3. Quantitative Estimation.

When copper is dissolved in nitric acid, and the solution does not contain any other metal or non-volatile substance, it is sufficient to evaporate the solution to dryness in a platinum or porcelain crucible, adding a slight excess of nitric acid to prevent reduction of the copper by any deoxidising substance that may be present, and heat the residue to redness. The copper then remains as protoxide, which must be weighed immediately after cooling, with the cover on the crucible, because it is very hygroscopic: 100 pts. of the oxide correspond to 79.82 per cent. of copper.

In other cases the copper must be separated by precipitation. This may be done in several ways.

a. By *caustic potash*, which, when added to a boiling solution of a cupric salt, throws down the copper as protoxide, in the form of a heavy black powder. Care must be taken not to add the potash in too great excess, as a small quantity of the copper will then be retained in solution. The precipitate is to be washed with boiling water, then dried on the filter, ignited in a porcelain or platinum crucible, and weighed with the same precautions as before. As a small quantity of the protoxide may have been reduced by the organic matter of the filter, it is best, after weighing, to moisten it with a few drops of nitric acid, then ignite and weigh again.

b. *Hypochlorite of sodium* may, in some cases, be advantageously used in place of caustic alkalis, to precipitate copper as protoxide. (Field, Chem. Soc. J. xiv. 159.)

c. When other metals are present, it is often necessary to precipitate the copper as sulphide, by *sulphydric acid*. In this case the precipitated sulphide must be washed as quickly as possible with water containing sulphydric acid, to prevent oxidation. The precipitate may then be dried, and the filter burnt with the precipitate on it, after which the precipitate is treated with strong nitric acid, which dissolves it, with separation of sulphur, and the copper is precipitated from the solution by potash as above. The chief precaution to be attended to in this process, is to wash the precipitated sulphide quickly, and to preserve it as completely as possible from contact with the air, otherwise the sulphide becomes partially oxidised and converted into sulphate, which, being soluble, runs through the filter; when this takes place, the filtrate becomes brown, because the copper thus carried through is again precipitated by the sulphydric acid in the filtered liquid.

From neutral or alkaline solutions, copper may also be precipitated by *sulphide of ammonium*, but this method is not quite so exact, because sulphide of copper is slightly soluble in that reagent, and the precipitate oxidises more quickly than that formed by sulphydric acid.

d. By *zinc or iron*. A very exact mode of estimating copper is to precipitate it from its solutions in the metallic state by means of pure zinc. The solution, which may contain sulphuric or hydrochloric acid, but should be free from nitric acid, is placed in a platinum capsule or crucible, previously weighed; a piece of zinc large enough to precipitate all the copper is immersed in it; and if the solution is neutral, hydrochloric acid is added in sufficient quantity to produce a moderately brisk disengagement of hydrogen, the vessel being covered with a watch-glass, to prevent splashing. The copper is immediately precipitated, partly on the platinum in a compact layer, partly in the spongy form. As soon as all the zinc appears to be dissolved, the precipitate must be pressed in different parts with a glass rod, to make sure that there are no little lumps of zinc remaining; the complete solution of the zinc may be insured by adding a few drops of hydrochloric acid, and observing whether any further evolution of hydrogen takes place. The clear solution is now to be decanted, and a drop of it tested for copper with ferrocyanide of potassium: if no coloration takes place, the precipitated copper may be washed with hot water by decantation, till the wash-water no longer gives a cloud with nitrate of silver; the greater part of the water in the crucible is then poured off, as much as possible of the remainder taken up by filter-paper, and the precipitated copper dried as rapidly as possible at 100° C., then left to cool and weighed. The precipitation may also be performed in a glass or porcelain vessel, but it is not so rapid as in platinum; it might, however, be accelerated by inserting a piece of platinum foil.

This process gives very exact results, provided the zinc used is perfectly pure; if, on the other hand, the zinc contains lead, or any other metal that will not dissolve in hydrochloric acid, that metal will mix with the precipitated copper and vitiate the result. It is necessary also to avoid using a piece of zinc much larger than is necessary, as in that case, after all the copper is precipitated, an electric circuit may be formed between this copper and the remaining zinc, which may cause a small portion of the dissolved zinc to be deposited on the copper in the metallic state, and to mix itself so intimately therewith, as to render its subsequent separation by hydrochloric acid very difficult. (H. Rose, *Chimie Analytique*, ii. 257.)



Iron is not so good a precipitant as zinc, because it always contains carbon, which remains undissolved and increases the weight of the precipitated copper (Rose). Moreover, unless a certain excess of hydrochloric acid is present, basic salts of iron are sure to be formed, which remain with the copper and increase its weight; and, on the other hand, if much free hydrochloric acid is present, a portion of the precipitated copper is likely to be dissolved in the form of cuprous chloride. (Field, Chemical News, i. 62.)

*e. Other modes of precipitation.*—The following methods have been recommended, but their results are, on the whole, not to be depended upon so much as those of the methods previously given. *a.* By *sulphocyanate of potassium*, in a neutral or slightly acidulated solution of copper, previously treated with an alkaline sulphite, to reduce the cupric salt to a cuprous salt. The precipitate, after being left to settle, is collected on a weighed filter, washed, dried at  $100^{\circ}\text{C}$ ., and weighed, the copper being calculated from the weight of the cuprous sulphocyanate,  $\text{CuCNS}$ , which contains, 52.5 per cent. copper (Rivot). According to Rose, the method is not quite exact, because the sulphocyanate of copper is slightly soluble in water. *b.* By boiling the cupric solution with *hyposulphite of sodium*. The copper is then completely precipitated as sulphide, provided the quantity of the reagent added be only just what is required; but an excess retains a portion of the copper in solution as cuproso-potassic hyposulphite. The method is therefore very uncertain. *c.* By *iodide of potassium*, which throws down cuprous iodide; but the precipitation is never complete. *d.* By introducing a weighed piece of metallic copper into a solution of a cupric salt supersaturated with ammonia, and diluted with de-aërated water, so as to completely fill the containing vessel, which is then tightly closed. A quantity of copper is thereby dissolved just sufficient to convert the cupric oxide,  $\text{Cu}^{\circ}\text{O}$ , in the solution into cuprous oxide,  $\text{Cu}^{\circ}\text{O}$ ,—that is to say, a quantity equal to that which previously existed in the solution. Hence, if the copper plate be weighed after the reaction is complete, the loss of weight gives the quantity of copper in the original solution. This method, given by Levöl, is a modification of Fuchs's method of estimating sesquioxide of iron. (See IRON, ESTIMATION OR.) According to H. Rose (*Chimie Analytique*, ii. 259), the quantity of copper which it gives is always too large.

When copper exists in solution, in the form of a cuprous salt, it may be oxidised by nitric acid, and then precipitated by either of the methods above given.

If a solution of copper contains organic matter, but no fixed inorganic substance, it may be evaporated to dryness, then calcined in a current of air, to burn off the organic matter and oxidise the copper, which may then be moistened with a drop of nitric acid, ignited, and weighed; or the organic matter may be destroyed by either of the processes given in connection with arsenic (i. 366).

#### Volumetric Methods of estimating Copper.

*Parkes's method*, by cyanide of potassium (*Mining Journal*, 1851).—When a solution of cyanide of potassium is slowly added to a blue ammoniacal solution of copper, the colour gradually becomes fainter and ultimately vanishes, in consequence of the formation of cupro-cyanide of ammonium. The reaction is complicated, several double cyanides of copper and ammonium being formed at first, but, according to Mohr, the ultimate result is the formation of the compound  $\text{CuCy.NH}_4\text{Cy}$ , containing 2 at. cyanogen to 1 at. copper. On this supposition, each atom of copper (31.6 grs.) in the solution will require 2 at. cyanide of potassium ( $2 \times 65 = 130$  grs.) to precipitate it.

To standardise the solution of cyanide of potassium, a known weight (5 to 10 grs.) of pure electrolyte copper is dissolved in nitric acid, the solution boiled to expel nitrous fumes, then diluted with water to about half a pint, and treated with ammonia in excess; and to the resulting blue liquid, the solution of cyanide of potassium is gradually added from the burette, till the deep blue colour is almost discharged and is replaced by a faint lilac tint. It is then left to stand for about twenty minutes, and if the colour does not completely disappear, a little more of the cyanide solution must be added from the burette, and the liquid again left to stand till the colour has disappeared. The number of burette divisions of the cyanide solution added will give the value in copper of a grain-measure (or of a cubic centimetre) of the solution. Thus, suppose that 200 divisions of the burette are equal to 1000 grain measures, and that 147.5 divisions of the solution are required to decolorise a solution containing 7.5 grains

of copper; then 200 such divisions would decolorise a solution of  $\frac{200}{147.5} \cdot 7.5 = 10.17$  grains of copper. By repeating this determination two or three times with different quantities of copper, the mean value of 200 burette divisions may be found. It is convenient to dilute the solution, so that 200 burette divisions shall correspond exactly to 10 grains of copper.



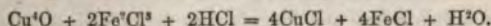
The standard solution of cyanide thus obtained is to be applied in exactly the same manner, to estimate the amount of copper in any given solution. Thus, suppose 37 grs. of a copper-alloy to be dissolved in nitric acid, and that the solution treated with excess of ammonia is decolorised, as above, by 320 burette divisions of the standard cyanide solution; then the quantity of copper in the 37 grs. of alloy is  $\frac{320}{200} \cdot 10 = 16$  grs., and the percentage of copper is  $\frac{16}{37} \cdot 100 = 43.2$  per cent.

This method is very extensively used for the assaying of copper ores. When carefully performed, it will give the amount of copper correctly within 0.1 or 0.2 per cent. It has also the great advantage of not being vitiated by the presence of iron in the solution. When this metal is present, the cyanide-solution should be added to the ammoniacal liquid *without filtering off the suspended ferric oxide*; for this oxide holds an ammoniacal solution of copper with such tenacity, that it cannot be completely separated, even by several hours washing with boiling water. The method may also be applied to the estimation of copper alloys and minerals containing tin, antimony, or arsenic, but not to such as contain zinc, nickel, cobalt, manganese, or silver, because these metals likewise form double cyanides. (Field, Chemical News, i. 25.)

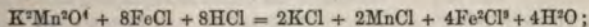
*Pelouze's method*, by sulphide of sodium.—The copper being dissolved in an acid, the solution is treated with excess of ammonia; and to the deep blue solution thus formed a solution of sulphide of sodium, of definite strength, is added. The copper is thereby precipitated in the form of an oxysulphide,  $\text{Cu}^2\text{O} \cdot 5\text{Cu}_2\text{S}$ . By adding the alkaline sulphide cautiously, it is easy to catch the precise moment when all the copper is precipitated, because the liquid at the same time becomes colourless. The quantity of the solution of the alkaline sulphide used indicates the quantity of copper present.

The exactness of this method is not diminished by the presence of iron, zinc, cadmium, tin, lead, or antimony, because the sulphide of sodium does not begin to act on these metals till the copper is completely precipitated; it is essential, however, that the iron be wholly in the state of sesquioxide. It is not necessary to separate the precipitate which some of these metals yield on the addition of ammonia, unless, indeed, it be very copious, in which case it might disguise the colour of the liquid. But the process is vitiated by the presence of cobalt, nickel, mercury, or silver; silver, however, and mercury, if in the state of mercurous oxide, may be easily separated by hydrochloric acid. According to some chemists, this process is liable to uncertainty from two causes: 1st. Because the oxysulphide of copper reduces a portion of the protoxide to hemioxide, thereby rendering the solution colourless before the precipitation is complete; 2ndly. Because a portion of the sulphide of sodium is oxidised and converted into hyposulphite. According to Field, however (Chemical News, i. 62), the process is very accurate, though somewhat tedious.

*F. Mohr's method*.—The copper-compound having been weighed and dissolved in acid, is mixed, in a porcelain basin, with neutral tartrate of potassium and excess of caustic potash, and then heated with a quantity of milk-sugar or honey, sufficient to precipitate all the copper as cuprous oxide, the completion of the precipitation being indicated by the brown colour which the liquid then acquires. The precipitated cuprous oxide is then filtered, washed with hot water, and gently heated, together with the filter, with a mixture of pure sesquichloride of iron and dilute hydrochloric acid. It is thereby dissolved in the form of protochloride of copper, the sesquichloride of iron being at the same time reduced to protochloride:



In the filtered liquid, diluted to a convenient strength, and heated to about  $30^\circ \text{C}$ ., the quantity of iron in the state of protochloride is determined by a graduated solution of permanganate of potassium (see Iron):



and thence the equivalent quantity of copper is readily determined. The presence of lead, zinc, bismuth, manganese, or iron, in the alkaline solution does not interfere with the process; silver or mercury must be separated before the precipitation of the cuprous oxide. (See i. 264.)

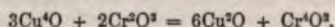
*Treill's method* (Compt. rend. xlv. 230).—This is similar to the preceding, excepting that the reduction of the cupric to cuprous oxide is effected by adding a solution of sulphite of sodium to the copper solution, previously supersaturated with ammonia. The excess of sulphurous acid is then expelled by boiling with hydrochloric acid, and the copper estimated by means of sesquichloride of iron and permanganate of potassium as above. This method is easier of execution than the preceding, inasmuch as grape-sugar is difficult to wash from the cuprous oxide.

*C. Mohr's method*.—The copper is precipitated from its neutral solution by metallic

iron ( $\text{Cu}^2\text{SO}^4 + \text{Fe}^2 = \text{Fe}^2\text{SO}^4 + \text{Cu}^2$ ), and the amount of iron in the solution estimated by means of permanganate of potassium.

*Fleitmann's method.*—The copper is also precipitated by iron, but the precipitate is washed and dissolved in sesquichloride of iron ( $\text{Fe}^2\text{Cl}^3 + \text{Cu} = 2\text{FeCl} + \text{CuCl}$ ), and the iron is determined by permanganate of potassium. This method gives good results. C. Mohr's process is less exact, and is quite inadmissible when iron is also present, as in the greater number of copper ores.

*Streng's method.*—The cupric oxide in the solution is reduced to cuprous oxide by grape-sugar; the precipitated oxide is dissolved in hydrochloric acid; a solution of starch and iodide of potassium are added; and afterwards a standard solution of acid chromate of potassium, till a blue colour is produced, indicating that the chromate is in excess:

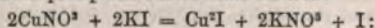


The amount of copper is calculated by the formula:

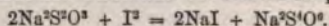
$$x = \frac{100 \cdot c \cdot C \cdot 12\text{Cu}}{\text{K}^2\text{O} \cdot 2\text{Cr}^2\text{O}^3 \cdot A} = \frac{37920 \cdot c \cdot C}{244 \cdot 4 \cdot A};$$

where  $C$  denotes the number of grains-measure of the chromic solution used;  $c$  the quantity of acid chromate of potassium in 1 grain-measure of the solution;  $A$  the weight of the cupriferous substance dissolved; and  $x$  the required percentage of copper.

*Brown's method.*—The copper solution is treated with iodide of potassium, whereby cuprous iodide is precipitated and iodine set free:



and the free iodine is removed by means of a standard solution of hyposulphite of sodium, whereby iodide and tetrathionate of sodium are produced:



The copper-compound, if solid, an alloy for instance, is dissolved in nitric acid; carbonate of sodium is added till a slight precipitate is formed, and the precipitate is re-dissolved in acetic acid (free nitric acid would vitiate the result by decomposing the iodide of potassium). A quantity of iodide of potassium is next added, equal to, at least six times the weight of the copper to be determined, and then the standard solution of hyposulphite in quantity sufficient to remove the greater part of the free iodine, which point will be indicated by the colour of the liquid changing from brown to yellow. Lastly a clear solution of starch is added, and the addition of the hyposulphite is cautiously continued till the blue colour of the iodide of starch is completely destroyed.—The solution of hyposulphite of sodium is graduated by dissolving a known weight of pure electrotypic copper in nitric acid, and proceeding as above, each atom of hyposulphite corresponding to 1 at. free iodine and to  $\frac{1}{2}$  at. copper, as shown by the preceding equations. This method of estimating the free iodine is similar in principle to that of Bunsen (i. 265). If the copper-compound contains a large quantity of lead or iron, these metals must be removed before commencing the determination, because the yellow colour of the iodide of lead and the red of the acetate of iron would interfere with the result (Chem. Soc. Qu. J. x. 71). The presence of iron might introduce another source of error, viz. that the sesquioxide of iron would be partially deoxidised by the hyposulphite of sodium. The estimation of copper by this method in many alloys is very rapid and trustworthy.

*Field's method.*—This process also depends upon the reaction of iodine on cuprous salts. When a solution of iodine in iodide of potassium is added to the solution of a cuprous salt, both the free iodine and that which is in combination unite with the copper. Hence, if the solution of a cupric salt free from nitric acid be reduced to the cuprous state, by mixing it with sulphite of sodium, the excess of sulphurous acid then expelled by boiling with hydrochloric acid, the solution mixed with starch when cold, and a standard solution of iodine in iodide of potassium added from a burette, cuprous iodide will be precipitated; and where the two solutions touch, a bright blue ring will be formed, which disappears at first on agitation, but becomes permanent when the decomposition is complete. An objection to this process, however, appears to be that the cuprous iodide has a great influence on the colour of the iodide of starch, rendering it paler and less distinct. (*Chemical News*, i. 74.)

*Scheff's method.*—This method is founded on the fact that a solution of sesquichloride of iron mixed with cuprous chloride is not coloured red by sulphocyanate of potassium. Hence, if a cupric solution be boiled with grape-sugar and alkali, till all the copper is precipitated as cuprous oxide, and this oxide be dissolved in hydrochloric acid, the amount of copper contained in it may be determined by adding a



standard solution of ferric chloride, till a drop of the liquid, placed on a white plate, is reddened by sulphocyanate of potassium.

The same method is applicable to the determination of the amount of cuprous oxide in a solution likewise containing cupric oxide. (Ann. Ch. Pharm. cxii. 372.)

#### 4. Separation of Copper from other Metals.

From the metals of the second and third groups (i. 217), and from all non-metallic elements, except selenium and tellurium, copper is easily separated by *sulphydric acid*, which throws it down as sulphide. From the metals of the first group (arsenic, antimony, &c.), and from selenium and tellurium, it may for the most part be separated by the insolubility of its sulphide in the *sulphides of the alkali-metals*. This method cannot, however, be depended upon for the separation of very small quantities of *arsenic* and *antimony* from copper. Bloxam has shown that it is altogether fallacious when the quantity of arsenic present does not exceed 1 per cent. of the copper. Of tin, much larger quantities may be overlooked, if the separation is based on the solubility of its sulphide in sulphide of ammonium. According to Fresenius, the separation of tin from copper is more easily effected by digesting the sulphide with yellow sulphide of sodium; but to render the separation complete, the digestion must be repeated three or four times.

*Antimony* is more easily separated from copper than arsenic or tin by means of sulphide of ammonium; but the method does not appear to be capable of detecting less than 0.03 per cent. of antimony in copper.

According to Abel and Field (Chem. Soc. J. xiv. 290) the separation of arsenic from copper may be much better effected by passing sulphydric acid gas, to complete saturation, through the solution of the two metals mixed with excess of ammonia; the copper is then precipitated while the arsenic remains in solution. In this manner  $\frac{1}{100}$  per cent. of arsenic may be detected in copper.

When the amount of arsenic is not less than 0.2 per cent. it may also be detected by digesting the sulphides in strong sulphide of ammonium for many hours.

For the detection and estimation of extremely small quantities of arsenic and antimony, such as are often met with in refined copper supposed to be pure (see Table, ii. 37), Abel and Field give the following process.

About 200 grains of the metal are dissolved in nitric acid, a small quantity of *nitrate of lead* is added, equal to about 10 grains of the salt, and subsequently an excess of ammonia and carbonate of ammonia. A precipitate is thereby formed which may consist of oxide, carbonate, arsenate, and antimonate of lead, and oxide of bismuth, the whole of the copper remaining in solution. The precipitate is separated by filtration, thoroughly washed, and digested in a strong solution of oxalic acid, which dissolves the arsenic and antimony. The filtrate is mixed with sulphide of ammonium; or, better, it is rendered alkaline by ammonia and sulphydric acid gas passed into it to saturation. Traces of sulphide of copper then generally separate; after they have been removed, the filtrate is diluted to 8 oz., and slightly acidulated with hydrochloric acid. If any larger amount of arsenic or antimony is present, an immediate precipitate will be formed; if not, the vessel should be exposed for a few hours to a temperature of 140° to 200° F., when the metals, if present, will appear as sulphides, the precipitate being orange-coloured or yellow, according as antimony is present or absent.

The precipitated sulphides are oxidised with strong nitro-muriatic acid, the clear solution is mixed with sal-ammoniac and excess of ammonia, and the arsenic is precipitated by sulphate of magnesium as ammonio-magnesian arsenate. The liquid filtered from this precipitate is slightly acidulated with hydrochloric acid and the antimony is precipitated by sulphydric acid as trisulphide, to be ultimately determined as tetroxide (i. 320). If the presence of antimony and arsenic has been previously ascertained, the precipitation of these metals as sulphides from their solution in oxalic acid may be dispensed with, and the arsenic at once precipitated as ammonio-magnesian arsenate.

A good method of separating copper from arsenic in the analysis of minerals is to evaporate the solution nearly to dryness, add *hypochlorite of sodium* in considerable excess, and boil for about 20 minutes. All the arsenic then dissolves as arsenic acid, while the copper is left behind as black-oxide. (Field, Chem. Soc. J. xiv. 159.)

From bismuth, copper may be completely separated by *cyanide of potassium*, which precipitates the bismuth as cyanide, and retains the copper in solution as potassio-cupric cyanide. If the solution contains a large excess of acid, it should be nearly but not quite neutralised with potash before the cyanide is added. The filtrate is boiled with hydrochloric acid containing a little nitric acid, to convert the copper into chloride, and the copper is then precipitated by potash. The two metals, if precipitated as sulphides, may also be separated by cyanide of potassium, which dissolves the sulphide of copper and leaves the sulphide of bismuth.



If the two metals are dissolved in nitric acid, and no sulphuric acid is present, the separation may be completely effected by adding hydrochloric acid, and then a large quantity of water, which throws down the whole of the bismuth as oxychloride. If the solution is very acid, it should first be concentrated by evaporation. If sulphuric acid is present, the separation must be effected by cyanide of potassium.

The old method of separating copper from bismuth by means of carbonate of ammonia, does not give exact results, some of the copper always remaining with the precipitated carbonate of bismuth, unless the solution and precipitation are repeated several times.

When bismuth and copper exist together in an alloy, they may be separated by heating the alloy strongly in a stream of chlorine. Chloride of bismuth then passes over, and may be received in water, while the copper remains as protochloride, which may be dissolved in water acidulated with nitric acid, and precipitated by potash. (H. Rose.)

For detecting the small quantities of bismuth often found in commercial copper and copper ores, the following method is advantageous. The copper being dissolved in nitric acid, a solution of nitrate of lead (about 5 parts of the salt to 100 of copper dissolved), is added, then ammonia and carbonate of ammonia; the precipitate is washed with ammoniacal water and dissolved in acetic acid; iodide of potassium is added in considerable excess, and the liquid is warmed till the precipitated iodide of lead is redissolved. On cooling, the iodide of lead will be deposited in crystalline scales, which, if free from bismuth, are of a pure gold-yellow colour, but if bismuth is present, assume a dark orange or crimson tint. This test is extremely delicate, even 0.00025 of a grain of bismuth in 100 grs. of copper imparting a dark orange tint to the iodide of lead, while 0.001 gr. imparts a reddish-brown tinge, and 0.01 gr. a bright crimson. (Abel and Field, *loc. cit.*)

From lead, copper may be completely separated by treating the solution with a mixture of *dilute sulphuric acid* and *alcohol*, which throws down all the lead as sulphate. The filtrate is then boiled to drive off the alcohol, and the copper precipitated by sulphydric acid.

The separation may also be effected by cyanide of potassium, in the manner above described for bismuth.

The separation of these two metals by carbonate of ammonia is never quite complete, still less by caustic potash.

For determining the small quantities of *lead* and *bismuth* found in commercial copper, Abel and Field give the following method, founded on that above described for the estimation of arsenic and antimony.

The nitric acid solution of about 200 grs. of the copper is mixed with a small quantity of solution of phosphate of sodium; ammonia is then added in excess, and the precipitate is purified from copper by washing with ammoniacal water. This precipitate is then dissolved in hydrochloric acid; the solution, rendered alkaline by ammonia, is treated with excess of sulphydric acid; the precipitated sulphides of lead and bismuth are thoroughly washed, and dissolved in dilute nitric acid; and the solution, nearly neutralised with ammonia, is digested with a small quantity of hydrated oxide or basic nitrate of copper, which precipitates the oxide of bismuth, while lead remains in solution. The washed precipitate is dissolved in nitric acid, and the bismuth is separated from the copper by ammonia; the oxide of bismuth thus obtained is purified by washing, and its weight determined in the usual way. The solution containing the nitrates of lead and copper is mixed with carbonate of sodium and excess of acetic acid, and the lead is precipitated as chromate by acid chromate of potassium. [It might also be precipitated by sulphuric acid and alcohol.] If the copper contains iron, that metal will be precipitated together with the bismuth. In this case, the precipitate must be redissolved in an acid, and the bismuth precipitated as sulphide by sulphydric acid.

From cadmium.—The best method of separating copper and cadmium is to mix the solution with *cyanide of potassium*, till the precipitate first formed redissolves, and pass sulphydric acid gas through the liquid. Sulphide of cadmium is then precipitated, while the copper remains dissolved as sulphide. The filtrate is then boiled with hydrochloric and a little nitric acid, till all the hydrocyanic acid is expelled and the copper is precipitated by potash.

Copper may also be separated from cadmium by *carbonate of ammonia*, in which carbonate of cadmium is insoluble; also by *sulphocyanate of potassium*, which precipitates the copper (ii. 58), but not the cadmium.

From silver, copper is separated by precipitating the silver as chloride.

For the separation of copper from mercury, gold, platinum, and the allied metals, see those metals.

## 5. Valuation of Copper Ores.

**I. By the dry way.**—The ordinary method of assaying copper ores, consists of a series of processes, similar in principle to the operations of smelting on the large scale. Oxidised ores and furnace-products, if moderately rich, are melted with black flux (a mixture of nitre and burnt tartar), whereby a button of metallic copper is obtained, which, if necessary, may be subsequently refined. Poorer oxidised ores and slags are first melted with iron pyrites, to obtain a regulus containing cuprous sulphide, which is then treated as below.

Sulphuretted ores and furnace-products, if rich, are first roasted in a muffle, to convert the sulphides into oxides. Poorer ores, like those of Cornwall, containing from 6 to 10 per cent. of copper, are first fused with a mixture of nitre and borax, whereby a portion of the sulphur is removed; the siliceous and earthy matters are separated in the form of a vitreous slag, and a button of regulus is obtained, containing the whole of the copper as sulphide, which may then be roasted. The roasted ore—or regulus—is next melted in a crucible, with black flux and a mixture of borax and glass; the more oxidable metals then pass into the slag, and the copper is reduced to a button of *coarse copper*, which may be refined either by fusing it with borax in a current of air, or by expelling it with lead.

This process does not yield very exact results, the percentage of copper which it shows being always less than that obtained by the wet method of assaying. For details, see *Uré's Dictionary of Arts, Manufactures and Mines*, i. 839; *Percy's Metallurgy*, i. 454.

**Plattner's method.**—This method, which is exact, but somewhat difficult of execution, serves to determine the quantities of copper, lead, bismuth, cobalt, and nickel, existing in ores, slags, alloys, &c.: it involves the following series of operations.

**a. Roasting.**—100 cents\* of the ore, containing sulphides or sulphates, is roasted on a roasting test (*fig. 142*), first *per se*, then with carbonate of ammonia, till all the sulphur is expelled. Ores containing gypsum, heavy spar, or alkaline sulphides, and in which the metals are united with sulphur or arsenic, are prepared for assaying by fusing 100 cents of the ore with 100 cents of vitrified borax or glass, and 10 cents of colophony, under a layer of 300 cents common salt, in a covered crucible heated for  $\frac{1}{2}$  to  $\frac{3}{4}$  hour, in a muffle or air-furnace: a regulus is thereby obtained containing the metals. If the metals are in the form of oxides, associated with gypsum or heavy spar, from 10 to 30 cents of metallic arsenic must be added to the preceding mixture. The sulphide of sodium, which is produced by the action of the sulphur on the borax, and passes into the regulus, is washed out with hot water.

Fig. 142.



**b. Conversion of the metals into Arsenides.**—The roasted ore or regulus is triturated with 100 cents of metallic arsenic, and heated for 8 or 10 minutes in a covered assay crucible (*fig. 143*), placed in a closed red-hot muffle, as long as combustible arsenic vapours are evolved. Some of the metals are thereby converted into arsenides, viz.  $\text{Cu}^{\text{I}}\text{As}$ ,  $\text{Pb}^{\text{I}}\text{As}$ ,  $\text{Co}^{\text{I}}\text{As}$ ,  $\text{Ni}^{\text{I}}\text{As}$ , and  $\text{Fe}^{\text{I}}\text{S}$ ; part of the iron is converted into ferroso-ferric oxide; undecomposed sulphate of lead into sulphide; antimonious oxide into arsenide of antimony; oxide of bismuth into arseniferous metallic bismuth, while the oxide of zinc remains unaltered.

Fig. 143.



Substances not originally containing sulphur, such as black copper, nickel-silver, slags containing cobalt and nickel, &c., are treated in the finely divided state (filed, laminated, or pulverised), in quantities of 50 to 100 cents, with 100 cents of metallic arsenic as above. The product is either a sintered button or a fused mass.

**c. Union of the resulting metallic arsenides into a whole, and separation of the Lead and Bismuth by fusion with appropriate fluxes.**—If the crucible used in the preceding operations is free from cracks, and gives a clear ringing sound when struck, the mass contained in it is covered with 10 to 20 cents of iron wire (according to the amount of lead present), a mixture of 200 cents of black flux, and 50 to 100 cents of vitrified borax (the quantity being greater as the amount of earthy matter in the assay is less), and the whole is covered with 300 cents of purified common salt, and a lump of charcoal. If the crucible has been injured in the preceding operations, a new one must be taken. The crucible, with its cover on, is heated in the

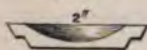
\* The cent here spoken of, is not the weight so-called by the Cornish assayers, (= 4 grains), but that which in German assaying is called a *pound*, 100 of which make a *Prober-centner*, equal to 375 grammes (or 57.56 grains) at Freiberg, and 3654 grammes in the Oberharz.



muffle-furnace for 25—30 minutes, or in the air-furnace rather longer, to a temperature gradually raised to the melting point of copper. A successful operation yields a well-fused slag of dark green to black colour, covered with a grey crust of common salt, and at the bottom a regulus, on which, if the substance under examination contains lead, that metal is found to have separated either on the bottom or at the side. In the former case, the lead is removed with the knife; in the latter, the regulus, with the lead side uppermost, is broken up in a mortar, the malleable lead then separating from the brittle arsenic compound, which is mixed with a few cents of colophony, and reserved for further treatment. The lead contains nearly all the silver in the ore, together with the bismuth and a little antimony, but no copper. If lead is absent, the bismuth separates in like manner on the surface of the regulus; but, being brittle, is not so easily separated from the arsenides. In this case, it is necessary to add from 10 to 20 cents of granulated lead, as well as 15—25 cents of iron; the excess then gives approximately the quantity of bismuth. It must, however, be remembered that about 4 per cent. of lead is lost in the process.

*d. Separation of the Arsenide of Iron and of the Zinc from the Arsenides of Cobalt, Nickel, and Copper by oxidising fusion on a Scorifier.*—The arsenides are placed,

Fig. 144.



together with 50 to 75 cents of borax, on a scorifier (fig. 144), surrounded with glowing coals at nearly a white heat, and fused at a strong heat with the muffle closed. After a minute or two the muffle is partially opened, and as soon as the assay has acquired a bright vaporising surface, it is brought a little nearer to the orifice of the muffle, and the temperature is so regulated that small films of oxide may form upon the surface, and pass into the borax. If the temperature is raised too high, the assay becomes bright, and if it be kept too low, the entire surface becomes oxidised. The process is complete when the surface becomes tranquil, and fumes of arsenic begin to escape. At that stage, the whole of the iron and zinc are separated, the latter by scorification and volatilisation. If the assay becomes covered with a crust before the temperature falls, there is a deficiency of borax, and the process must be repeated on a new scorifier with fresh borax. The button thus obtained is left to cool partially, then completely quenched in water, and carefully cleaned from slag by tapping it with a hammer. If the assay has been removed from the muffle at the proper time, the slag will be quite free from cobalt, nickel, and copper.

*e. Removal of the excess of Arsenic by volatilisation.*—The metallic button still contains excess of arsenic, which is expelled by mixing it, according to its size, with  $\frac{1}{2}$  to 1 cent of borax-glass; laying it, wrapped up in thin paper, on a lump of charcoal having a cavity about half an inch deep, or on a scorifier made of powdered coke and pitch; melting it in a closed muffle; and, when the metal exhibits a shining surface, and begins to give off arsenic vapours, exposing it, with the muffle open, to a moderate heat till it no longer gives off vapours of arsenious acid with rapidity, and such vapours are no longer perceptible on taking the scorifier out of the muffle. The button, which then solidifies with a dull black surface, is weighed; it contains the definite compounds,  $\text{Co}^{\text{As}}$ ,  $\text{Ni}^{\text{As}}$ , and  $\text{Cu}^{\text{As}}$ .

The borax-glass dissolves the basic arsenite of cobalt, which is apt to form on the surface of the melted assay if the temperature is not kept high enough, and might hinder the volatilisation of the excess of arsenic. This salt is again reduced to the metallic state as soon as it comes in contact with the carbonaceous support.

*f. Separation of the Arsenides of Cobalt from the Arsenides of Nickel and Copper, and determination of the amount of Cobalt.*—The weighed button of regulus wrapped up in paper, is laid upon a scorifier containing from 10 to 30 cents of borax, surrounded with hot coals and heated nearly to whiteness; the muffle is closed; and the assay quickly brought to coruscation. The scorifier is then brought nearer to the opening of the muffle; a few pieces of charcoal are laid in front of it; and the arsenide of cobalt, which is the most oxidable of the three arsenides present, is left to be scorified by the borax,—at a temperature at which the fused assay exhibits a clean but not specular surface,—till the surface becomes covered with a green film of arsenite of nickel. If the substance under examination does not contain cobalt, this appearance is observed in the preceding operation, *e*. The loss of weight which the regulus has sustained, consists of  $\text{Co}^{\text{As}}$ , containing 61 per cent. of cobalt.

*g. Separation of the Arsenide of Nickel from the Arsenide of Copper.*—To scorify the arsenide of nickel, the button of regulus still containing  $\text{Ni}^{\text{As}}$  and  $\text{Cu}^{\text{As}}$ , is treated with borax in the manner above described, till the melted metal becomes bright, no more green films forming on its surface, and it begins to give off arsenic vapours from the decomposition of the arsenide of copper. The chief point to be attended to in this operation is the due regulation of the temperature, which must be lower in proportion as the assay contains a larger proportion of the easily fusible ar-



senide of copper. The loss of weight consists of  $\text{Ni}^4\text{As}$ , and a portion of arsenic volatilised from the arsenide of copper; the nickel cannot, therefore, be calculated directly from this loss, but must be estimated after the amount of copper has been determined. The separation of the arsenide of nickel from the arsenide of copper may be effected with sufficient accuracy, even if the proportion of copper is below 1 per cent.

*h. Volatilisation of the Arsenic combined with the Copper, and determination of the proportions of Nickel and Copper.*—The button of regulus, wrapped up in paper, is laid upon a glowing charcoal scorifier; the muffle is closed for a while; and as soon as the button is fused, the scorifier is brought near to the mouth of the muffle, which is heaped up with red-hot coals to the height of about  $1\frac{1}{2}$  inch; and the assay is kept at a temperature about equal to that required for the cupellation of silver, till films of basic cuprous arsenite begin to show themselves here and there on the clean surface of the metal. It is then exposed to a higher temperature, till it exhibits the bluish green colour of pure copper, and the films which form upon it, make their appearance no longer on the sides, but at the top. The assay is then taken out of the fire and cooled. The button of copper, whatever its colour and texture, must be malleable, and have a small quantity of cuprous oxide on its surface.

The weight of the copper button gives directly the proportion of copper in the assay. To determine the nickel, the copper is calculated as  $\text{Cu}^2\text{As}$ ; the resulting weight is deducted from the known weight of the arsenides of nickel and copper together, and the difference gives the weight of the  $\text{Ni}^4\text{As}$ , which contains 61 per cent. of nickel.

The process of assaying just described may be greatly shortened if one or more of the metals above considered are absent. If, for example, the cupriferous substance is free from nickel and cobalt, as is the case with most copper ores and many products obtained in copper smelting, the operations *f* and *g* become unnecessary, and the process is reduced to the separation of arsenide of iron, including more or less antimony and zinc (*e*) from the arsenide of copper, and the separation of the arsenic from the copper by volatilisation. (Plattner, *Beitrag zur Erweiterung der Probirkunst*, Freiberg, 1849; *Kerl's Hüttenkunde*, ii. 140.)

*II. Assaying of Copper Ores in the wet way.*—The ore being dissolved in nitric acid, the determination of the copper may be made by either of the methods given on pages 57—60. Of the methods by *weight analysis*, however, the one that is generally, indeed almost exclusively, employed, is the precipitation of the copper by iron, as it has the advantage of not requiring any special treatment for separating the copper from the iron in the ore. More exact results would be obtained by the use of pure zinc as the precipitant (p. 57).

Of the *volumetric methods*, that of Parkes is the one most generally used for the valuation of copper ores, as it likewise is not interfered with by the presence of iron, which nearly all these ores contain. Brown's process is exact and expeditious, but it requires the removal of iron and lead. It is, however, unaffected by the presence of arsenic, antimony, tin, or zinc, and is therefore very useful for the analysis of alloys.

An expeditious method of obtaining an approximate estimate of the quantity of copper in an ore or slag, is to dissolve a given quantity of it in nitric acid, mix the solution with excess of ammonia, and compare the colour with those of a series of standard solutions, prepared in a similar manner. (Jacquelin.)

#### 6. Atomic Weight of Copper.

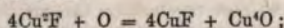
The atomic weight of copper has been determined by reducing a weighed quantity of the protoxide with hydrogen, and weighing the residual metal. In this manner, Berzelius, in 1820 (*Pogg. Ann.* viii. 182), obtained, as a mean of two experiments, the number 31.65. Erdmann and Marchand (*J. pr. Chem.* xxi. 385) found, as a mean of five closely agreeing experiments, made with cupric oxide obtained from the nitrate, the number 31.73, which may be received as very near the truth. Dumas (*Ann. Ch. Phys.* [3] lv. 129) by the same method, and from the weight of cuprous sulphide produced from a given quantity of copper, obtained numbers varying between 31.5 and 32.1, whence he regards 31.75 as the true atomic weight.

**COPPER, EMERALD.** Syn. with Dioptase.

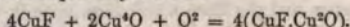
**COPPER, FLUORIDES OF.** *Protofluoride of Copper*, or *Cupric Fluoride*, is formed by dissolving cupric oxide or its carbonate in excess of aqueous hydrofluoric acid (metallic copper is not sensibly dissolved by the acid), and evaporating the resulting blue solution. As the excess of acid goes off, small, light blue crystals separate from the liquid. If the quantity of cupric carbonate is sufficient to neutralise the greater part of the acid, the compound separates out during the digestion: with a still larger quantity of carbonate, the oxyfluoride  $\text{Cu}^2\text{F}^2\text{O} + \text{H}^2\text{O}$  is formed (Berzelius). The crystals, which are but sparingly soluble in cold water, are decomposed by hot

water, yielding an acid solution and the insoluble oxyfluoride. The crystals heated with sulphuric acid yield 116 per cent. of cupric sulphate, and when ignited with excess of lead-oxide give off 26.3 per cent. of water (Berzelius). Protofluoride of copper combines with the fluorides of the alkali-metals, forming black compounds.

The *Hemifluoride*, or *Cuprous Fluoride*,  $\text{Cu}^2\text{F}$ , is obtained by treating cuprous oxide with aqueous hydrofluoric acid, washing the product with alcohol, then pressing and drying. It is a red powder, which melts when heated, appearing black while in the liquid state, but recovering its red colour on cooling. In the dry state it is permanent in the air; but when moist it is converted, first into a yellow mixture of cupric fluoride and hydrated cuprous oxide:



and afterwards into green cupric oxyfluoride:

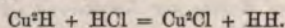


It is insoluble both in water and in excess of hydrofluoric acid, but soluble in strong hydrochloric acid. In the latter it forms a black solution, from which it is precipitated by water in the form of a powder, which is white at first but afterwards becomes rose-coloured. (Berzelius, Pogg. Ann. i. 21.)

*Borofluoride of Copper*,  $\text{CuBF}^4$  (see i. 634).

**COPPER, GREY.** (See TETRAHEDRITE).

**COPPER, HYDRIDE OF.**  $\text{Cu}^2\text{H}$ . When a solution of cupric sulphate is heated with hypophosphorous acid to about  $70^\circ\text{C}$ ., hydride of copper is deposited as a yellow precipitate, which soon turns red-brown. It gives off hydrogen when heated; takes fire in chlorine gas; and when treated with hydrochloric acid, is converted into cuprous chloride, with evolution of a double quantity of hydrogen, the acid giving up its hydrogen as well as the copper-compound:

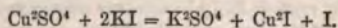


This action is remarkable, inasmuch as metallic copper is but very slowly acted upon by hydrochloric acid. It affords, indeed, a striking instance of the polarity of atoms alluded to in the articles CHEMICAL AFFINITY (i. 857), and CONTACT ACTION (ii. 12).

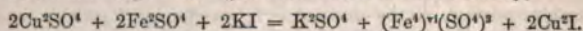
**COPPER, INDIGO.** See COPPER, SULPHIDES OF (p. 74).

**COPPER, IODIDES OF.** *Cupric Iodide*,  $\text{CuI}$ , is not known in the free state. An *ammonio-cupric iodide*,  $2(\text{CuI}.2\text{NH}^3) + \text{H}^2\text{O}$ , is produced when cuprous iodide, moistened with ammonia, is exposed for some time to the air, a blue solution being then formed, which, when mixed with alcohol, yields small, dark-blue tetrahedrons of the ammonio-iodide (Rammelsberg, Pogg. Ann. xlviii. 162). According to H. Hahn, it forms crystals belonging to the trimetric system, with the faces  $\infty \text{P} \infty . \infty \text{P} . \text{P} \infty . \frac{2}{3} \text{P} \infty . \frac{1}{3} \text{P} \infty . \text{P}$ . Ratio of axes = 0.3362:1:1.462 (Jahresber. d. Chem. 1859, p. 217). According to Berthelot, the same compound is obtained by mixing a concentrated ammoniacal solution of ammonio-cupric chloride, or sulphate, with iodide of potassium. It is soluble, without decomposition, in ammonia and in a small quantity of water, but a large quantity of water, especially if hot, decomposes it, with separation of a green oxyiodide. Alcohol and ether do not act upon it in the cold, but decompose it when heated. This compound exposed to the air gives off ammonia, and leaves green oxyiodide. When heated, it first gives off iodide of ammonium, then detonates and leaves a brown-red residue containing cuprous iodide.

*Cuprous Iodide*,  $\text{Cu}^2\text{I}$ , is produced: 1. By heating finely divided copper with iodine. 2. By precipitating a solution of cuprous chloride in hydrochloric acid with iodide of potassium, or by adding iodide of potassium to the solution of a cupric salt mixed with sulphite or hyposulphite of sodium. 3. By precipitating a dissolved cupric salt with iodide of potassium, half of the iodine being set free:



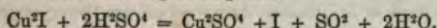
The precipitate must be washed with alcohol, to free it from adhering iodine. 4. By precipitating the aqueous solution of 1 at. cupric sulphate and at least 1 at. ferrous sulphate, with iodide of potassium (Soubeiran, J. Pharm. xii. 427);



Cuprous iodide, obtained by precipitation, is a brownish-white powder. When heated, it gives off 4 per cent. of water,—agreeing with the formula  $2\text{Cu}^2\text{I.H}^2\text{O}$ ,—and at a red heat fuses into a brown mass, which yields a green powder. It is but



imperfectly decomposed by ignition in a stream of *hydrogen gas* (H. Rose, Pogg. Ann. iv. 110). When ignited with *peroxide of manganese*, it is resolved into iodine vapour and cupric oxide (Soubeiran). With *nitric acid*, it yields vapour of iodine, nitric oxide gas, and cupric nitrate; and with *strong sulphuric acid*, it yields iodine vapour, sulphurous acid gas, and cupric sulphate:



Cuprous iodide boiled with *water*, and *zinc*, *tin*, or *iron*, yields metallic copper and a dissolved iodide of the other metal (Berthelot, J. Pharm. xiv. 614). *Aqueous fixed alkalis* form metallic iodides and separate cuprous oxide; a similar reaction is produced by *carbonate of potassium* or *sodium*, carbonic acid being likewise evolved. Cuprous iodide is not decomposed by *baryta*, *strontia*, *lime*, or *alumina*. (Berthelot).

*Ammonio-cuprous iodide*.  $\text{Cu}^{\text{I}}\text{I}2\text{NH}^{\text{S}}$ . When dry ammonia-gas is passed over cuprous iodide, the compound absorbs ammonia, becoming hot, and acquiring a brown colour; but on applying a gentle heat, the whole of the ammonia is driven off (Rammelsberg). When plates of copper are enclosed in a bottle together with a cupric salt strongly supersaturated with ammonia, the liquid being frequently shaken till it loses its colour, and then poured into a bottle containing aqueous iodide of potassium, which must be afterwards closed, ammonio-cuprous iodide separates, partly in colourless shining prisms, partly as a white crystalline powder. It cannot be dried without decomposition, as it gives off ammonia when exposed to the air. The colourless liquid from which the compound has separated, turns blue in the air from formation of ammonio-cupric iodide. (Levol, J. Pharm. [3] iv. 328.)

**COPPER, NITRIDE OF.**  $\text{Cu}^{\text{S}}\text{N}$ . This compound is formed, together with *water*, when dry ammonia-gas is passed over very loosely coherent cupric oxide heated to  $250^{\circ}\text{C}$ . The product, which generally contains more or less undecomposed oxide, and sometimes a little nitrate, is a dark green, sometimes nearly black powder, which at  $300^{\circ}\text{C}$ . is resolved into its constituents, with slight explosion. The temperature at which this decomposition takes place varies, however, with the nature of the surrounding gas; in oxygen gas it takes place at comparatively low temperatures; in air it requires a higher temperature, and in ammonia gas still higher. *Sulphuric acid* decomposes it with violence, giving off nitrogen and leaving metallic copper; other acids act in a similar manner, those which, like *nitric acid*, oxidise the copper, acting still more violently. In dry *hydrochloric acid gas* it yields sal-ammoniac and cupric chloride. *Chlorine* produces cupric chloride, with evolution of nitrogen. *Aqueous ammonia* does not appear to eliminate gas from the compound, but becomes blue by contact with it. (Schrötter, Ann. Ch. Pharm. xxxvii. 131.)

When dry ammoniacal gas is passed over red-hot copper, the copper becomes crystalline and brittle, but does not appear to take up any gas (Gm. v. 444). From Dick's experiments, it appears that copper is not rendered brittle by heating in ammonia-gas, unless it contains cuprous oxide, in which case the brittleness appears to be due to the porosity resulting from the reduction of the oxide by the hydrogen of the ammonia. (Percy's Metallurgy, i. 278.)

When a ball of copper connected with the positive pole of a six-pair Grove's battery is made to dip into one end of a long glass trough containing solution of sal-ammoniac, and a platinum plate connected with the negative pole into the other end, the sal-ammoniac being kept in excess, the liquid becomes blue, and a nitride of copper collects at the negative pole, in the form of a chocolate-coloured aggregation, which, after washing and drying, has a density of 5.9. Ten grains of this substance give off 0.214 cubic inches of nitrogen gas when heated, leaving metallic copper. (Grove, Phil. Mag. [3] xix. 100.)

**COPPER, ORES OF.** (See page 19.) The following synonymes require special notice:

Black Copper ore	.	.	Native black oxide.
Blue Copper ore	.	.	Azurite or blue carbonate (i. 783).
Emerald Copper ore	.	.	Diopside, $\text{Cu}^{\text{S}}\text{SiO}^{\text{S}} + \frac{2}{3}\text{aq}$ . (See SILICATES.)
Grey Copper ore	.	.	Tetrahedrite (q. v.)
Green Copper ore	.	.	Malachite or green carbonate (i. 783).
Indigo Copper ore	.	.	Native protosulphide (ii. 74).
Octahedral Copper ore	.	.	Native red oxide (ii. 70).
Variegated Copper ore	.	.	Purple copper (ii. 80).
Velvet Copper ore	.	.	Native sulphate of copper and aluminium. (See LETTSOMITE and SULPHATES.)
Yellow Copper ore	.	.	Copper pyrites (ii. 79).

**COPPER, OXIDES OF.** *a. Protoxide or Cupric oxide,  $\text{Cu}^2\text{O}$  or  $\text{CuO}$ .* *Black oxide of copper; Dutoxyde de cuivre; Kupferoxyd.*—This oxide is found native as *Melaconite* or *Black Copper* (*Kupferschwärze*). It occurs abundantly at Keweenaw Point, Lake Superior, in cubes (perhaps pseudomorphs of red copper ore), with truncated angles; more generally massive. Specific gravity, 6.26 (Whitney), 5.952 (Rammeisberg). Hardness = 3. Colour, dark steel grey in the crystals, black or greyish-black when massive.

Cupric oxide is prepared: 1. By continued ignition of copper in contact with the air. 2. By exposing cupric sulphate to an intense red heat, or the carbonate or nitrate to a moderate red heat. A convenient mode of preparing it for use in organic analysis is to ignite copper smithy-scales, moistened with a sufficient quantity of nitric acid to convert the whole of the metal and red oxide into black oxide. As thus obtained, it is less hygroscopic than when prepared by igniting the nitrate. The heat must not be raised too high, or the oxide will fuse, and will then be difficult to pulverise.—3. According to Ficinus, cupric oxide may be easily prepared by exposing a mixture of 1 pt. copper filings and 2 pts. deliquesced cupric nitrate to the air, till the whole is converted into a basic salt, and then igniting this salt.—4. When caustic potash is added by drops to a boiling solution of a cupric salt till the acid is saturated, the whole of the copper is precipitated as anhydrous black oxide, which may be freed from potash by washing with boiling water.

Cupric oxide prepared as above has the form of brown-black brittle scales and granules, or of a brownish-black powder, which, when strongly heated, assumes for a while a pure black tint. At a full red heat, it melts and solidifies to a mass having a crystalline fracture. By heating it to commencing redness in a silver crucible with from 4 to 6 times its weight of hydrate of potassium, washing the fused mass with water, and separating the flocculent cupric oxide from the crystalline portion by levigation, it may be obtained in regular tetrahedrons having a strong lustre. (Becquerel, *Ann. Ch. Phys.* li. 122.)

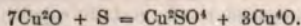
Jenzsch (Pogg. *Ann.* cvii. 647) found crystals of cupric oxide imbedded in cavities in the hearth of a calcining furnace at Freiberg; they were iron-black, shining, of specific gravity 6.451, nearly as hard as fluor-spar, and belonged to the trimetric system, exhibiting the faces  $\infty\text{P}$ ,  $\text{P}$ ,  $\infty\text{P}$ ,  $\text{P}$ ,  $\infty\text{P}$ ,  $\frac{1}{2}\text{P}$ . Inclination of faces:  $\infty\text{P} : \infty\text{P} = 99^\circ 39'$ ;  $\infty\text{P} : \text{P} = 113^\circ 58'$ ;  $\infty\text{P} : \text{P} = 122^\circ 58'$ . They were all twin-crystals, the face of combination being  $\infty\text{P}$ .

Cupric oxide is reduced to the metallic state by gentle ignition with *hydrogen* or *charcoal*; by hydrogen even at the temperature of boiling linseed oil. (Schrötter.)

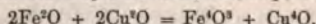
It is likewise reduced to the metallic state by *potassium* and *sodium*, at temperatures somewhat below the melting points of those metals, and with vivid incandescence. With fused *cyanide of potassium* it yields copper and cyanate of potassium (Liebig). When gently ignited with *metallic copper*, it is converted into cuprous oxide. With phosphorus at a red heat, it yields phosphide and phosphate of copper. Mixed with *phosphoric oxide*, it detonates slightly on the approach of a red-hot coal, and is converted into cupric phosphate and brightly glowing fused globules of phosphide of copper (Leverrier). A mixture of cupric oxide with excess of *sulphur* is resolved at a red heat into cuprous sulphide, sulphurous anhydride, and a trace of cupric sulphate:



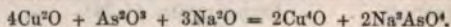
If, on the contrary, the cupric oxide is in excess, cuprous oxide and cupric sulphate are produced, and only a trace of sulphurous anhydride, excepting when the heat is raised to the point at which the cupric sulphate is decomposed (Max Jordan, *J. pr. Chem.* xxviii. 222):



When protoxide of copper is boiled with a solution of *stannous chloride*, stannic oxide is precipitated, and cuprous chloride dissolved (Proust; A. Vogel, *Kastn. Arch.* xxiii. 85). *Hydrated ferrous* and cupric oxides are converted by mutual decomposition into hydrated ferric and cuprous oxides; the latter of which may be dissolved out by ammonia (Levol, *Ann. Ch. Phys.* lx. 320; also *J. pr. Chem.* xiv. 115):



In presence of potash or soda, and with the aid of heat, cupric oxide is decomposed by *arsenious anhydride*, the products being cuprous oxide and arsenate of potassium. The decomposition is effected by mixing 160 pts. (2 at.) of cupric oxide with 100 pts. (rather more than  $\frac{1}{2}$  at.) of arsenious anhydride, and with excess of soda, and digesting the mixture at a gentle heat, with frequent agitation, till all the protoxide of copper is converted into hemioxide: the solution contains arsenate of sodium:





When ammonia is used in place of soda, only half of the protoxide of copper is converted into hemioxide: the rest remains dissolved in the ammonia, forming a blue solution, and no decoloration takes place till potash or soda is added. A mixture of arsenious acid with carbonate of potassium or sodium or quick-lime does not convert the protoxide of copper into the hemioxide (Bonnet, Pogg. Ann. xxxvii. 300). When protosulphide of iron is fused with protoxide of copper, sulphide of copper is formed (Karsten). Protoxide of copper is reduced to the state of hemioxide by boiling it with various organic substances, e. g. with oil of turpentine.

*Hydrated Cupric Oxide*, or *Cupric Hydrate*,  $\text{CuHO}$ , or  $\text{CuO.HO}$ , is formed by precipitating a dissolved cupric salt in the cold, with a slight excess of dilute caustic potash, quickly washing the blue precipitate with cold water, and drying it at the ordinary temperature of the air. The hydrate generally turns black from admixture of anhydrous cupric oxide, even during the washing and drying. According to Palmstedt, it is more durable when obtained by the action of caustic potash on carbonate of copper previously well washed with water. After drying, it forms greenish-blue friable lumps, having a conchoidal fracture; its taste is strongly metallic. In the dry state it remains undecomposed, even at  $100^{\circ}\text{C}$ ., but at a somewhat higher temperature it is converted into anhydrous black oxide; thus, if the hydrate be heated on paper, the change takes place at a temperature not high enough to char the paper. It is converted into the black oxide, with considerable diminution of volume, when kept for some time under water; also, by boiling in solution of caustic potash. Alcohol does not decompose the hydrate, either in the fresh or in the dry state (Proust, Ann. Ch. Phys. xxxii. 41). Much of the *Blue verditer* or *Bremen green* which occurs in commerce, consists of hydrated cupric oxide, prepared by precipitating a solution of sulphate of copper with caustic potash of  $15^{\circ}\text{B}$ ., washing the precipitate, again treating it with caustic potash of  $15^{\circ}$ – $18^{\circ}\text{B}$ ., and lastly washing it thoroughly. The potash-solution must contain a little carbonic acid, in the state, in short, in which it is obtained by slaking 50 pts. of lime in an aqueous solution of 80 pts. of pearlsh; otherwise the colour will be spoiled. (Gentele.)

According to Frémy (Ann. Ch. Phys. [3] xxiii. 161), hydrated cupric oxide, obtained by precipitating a solution of cupric sulphate in the cold with a large excess of potash, and then drying in vacuo, contains  $\text{Cu}^2\text{H}^2\text{O}^2$ , or  $\text{CuO.2HO}$ .

*Cupric Oxygen-salts*.—Cupric oxide has a strong affinity for acids, dissolving in them easily, and with evolution of heat, even after ignition; the hydrate and carbonate dissolve with still greater facility. The last-mentioned compounds likewise dissolve in ammoniacal salts, and liberate the ammonia on boiling. The anhydrous cupric salts are mostly white; the hydrated salts have a blue or green colour. They are for the most part soluble in water, and the solutions have a metallic taste and redden litmus. At a red heat they give off their acid, provided the acid is volatile; the sulphate, however, requires a strong heat to decompose it. For their behaviour with reagents and before the blowpipe, see page 55.

*Ammonio-cupric Oxide*.—Cupric oxide appears to unite with ammonia in more than one proportion. A dark azure-blue liquid is formed by exposing an ammoniacal solution of cuprous oxide to the air; or by bringing copper filings in contact with aqueous ammonia and a sufficient quantity of air,—or cupric oxide, either anhydrous or hydrated, with aqueous ammonia; or by allowing aqueous ammonia mixed with a few drops of sal-ammoniac solution to trickle through copper-turnings. If all acids, even carbonic acid, be excluded, the ammonia, according to Berzelius, appears to dissolve scarcely a trace of the anhydrous oxide; but on adding a drop of the solution of an ammoniacal salt, the oxide is abundantly dissolved (compare Wittstein, Repert. lvii. 32). The product is a dark azure-blue liquid. Phosphorus decolorises it, by forming a compound of cuprous oxide and ammonia, and ultimately precipitates the copper in the metallic state; zinc and cobalt likewise precipitate the copper. Iron reduces the copper imperfectly; arsenic, tin, and cadmium reduce it sparingly, and lead exhibits but mere traces of reduction (Fischer, Pogg. Ann. viii. 492). According to Wetzlar (Schw. J. l. 101), iron exerts no action on the pure solution, but slowly precipitates metallic copper from the solution mixed with sal-ammoniac, common-salt, nitre, or sulphate of potassium, nodules composed of copper and ferrous hydrate forming on its surface at isolated points, and extending till the liquid is decolorised. A large excess of ammonia prevents this precipitation, especially if the solution be mixed with nitrate or sulphate of potassium. Sulphurous acid added to the solution of cupric oxide in ammonia, throws down nearly all the copper in the form of red-brown cuprous oxide, containing small portions of sulphurous acid [and ammonia?] (A. Vogel). The liquid, when diluted with a large quantity of water deposits the cupric oxide in the form of hydrate. Potash—of which a larger quantity is required in proportion as the ammonia is in greater excess—likewise precipitates the cupric oxide, at least after a while, in the form of hydrate



[containing potash?], the precipitation, according to Berzelius, being complete; on boiling the liquid, black oxide of copper is immediately precipitated.

When ammonia, not in excess, is added to cupric salts, the precipitate usually consists of a basic salt free from ammonia; Kane, however (Ann. Ch. Phys. [2] lxxii. 283), on one occasion, by precipitating a solution of cupric chloride with ammonia, obtained a blue precipitate resembling hydrated cupric oxide, which was easy to wash, and did not lose ammonia during the washing. This precipitate underwent no change at  $149^{\circ}\text{C}$ .; but at a somewhat higher temperature, it was decomposed with a slight hissing noise, yielding nitrogen gas, ammonia, a large quantity of water, and a red mixture of copper and cuprous oxide. It was found to be free from chlorine, and to consist of  $4\text{NH}^3 \cdot 3\text{Cu}^2\text{O} + 6\text{H}^2\text{O}$ .

Malaguti and Sarzeau (Ann. Ch. Phys. [3] ix. 431) obtained the compound  $4\text{NH}^3 \cdot \text{Cu}^2\text{O} + 4\text{H}^2\text{O}$ , in fine blue crystals by passing ammonia-gas to complete saturation through water in which basic cupric chromate was suspended, crystallising out a portion of the cupric chromate, and leaving the mother-liquor under a bell-jar together with a mixture of slaked lime, sul-ammoniac, and lumps of quick-lime, so that it might evaporate in an atmosphere of ammonia. Blue crystals of basic cupric chromate then formed, together with green crystals of ammonio-cuprous oxide. These crystals deliquesce and give off ammonia when exposed to the air, and when heated, decompose with incandescence, leaving metallic copper. When a number of them lying together are heated, so that one begins to glow, the incandescence extends to the others, and vermicular tubes of copper are formed, covered here and there with oxide.

The solution of cupric oxide in ammonia, also the ammoniacal solution of basic cupric sulphate or hyposulphate, dissolves cellulose (cotton, linen, hemp-fibre, paper, &c.), this solvent power increasing with the amount of copper in the solution, and the cellulose is precipitated in the amorphous state by acids, salt, sugar, &c. (Schweizer, J. pr. Chem. lxxii. 109; lxxvi. 344; Peligot Compt. rend. xlvii. 1034.) According to Erdmann (J. pr. Chem. lxxvi. 385), the cellulose is not actually held in solution, but merely swollen and held in suspension, like starch in water (i. 820).

**HEMOXIDE OF COPPER, OR CUPROUS OXIDE,  $\text{Cu}^1\text{O} = \text{Cu}^2\text{O}$ , or  $\text{Cu}^2\text{O}$** , also called *Dioxide*, *Suboxide*, and *Red oxide of copper* (*Protoxide de cuivre*, *Kupferoxydul*).—This oxide is found native in two forms; 1. Red copper, (*Rothkupfererz*), which occurs crystallised in the regular system, generally in octahedrons and with octahedral cleavage; also massive, granular, sometimes earthy. Specific gravity = 5.85–6.15. Hardness = 3.5–4. Colour red, of various shades, with adamantine, submetallic, or earthy lustre; subtransparent or subtranslucent; occasionally crimson-red, by transmitted light. Streak brownish red, shining. Fracture conchoidal, uneven. Brittle. It occurs in the Bannat, in Thuringia, in Tuscany, in the Isle of Elba in cubes; in Cornwall, at Chessy, near Lyons, where crystals sometimes an inch in diameter are found embedded in lithomarge; at Ekatherinenburg in Siberia; abundantly in South Australia; in the Lake Superior region, and several other localities in North America. When found in large quantities, it forms a valuable ore of copper (Dana, ii. 101).—2. As Copper-bloom, Chalotrichite, or Capillary red oxide of copper (*Kupferblüthe*), which crystallises in the trimetric system, forming prisms with the acute and obtuse edges truncated; observed planes,  $\infty P \cdot \infty \bar{P} \cdot \infty \bar{P}$ . It is usually found in fine capillary crystallisations, grouped or reticulated. Cleavage rhomboidal, perfect. Specific gravity = 5.8. Colour cochineal and crimson-red. Occurs at Rheinbreitenbach, Moldawa, and Nischne Tagilsk. (Dana, ii. 122.)

**Preparation.**—1. By igniting 4 pts. of copper filings with 5 pts. of the protoxide, or 29 pts. copper filings with 24 pts. anhydrous cupric sulphate.—2. By heating 100 pts. of crystallised cupric sulphate with 57 pts. of crystallised carbonate of sodium, till the water of crystallisation is entirely expelled, and heating the residue to bright redness with 25 pts. copper filings.—3. A mixture of 5 pts. cuprous chloride (obtained by evaporating a solution of cupric chloride and fusing the residue) and 3 pts. anhydrous carbonate of sodium is fused at a gentle heat, and the cooled mass is lixiviated with water to dissolve out the sodium-salts: cuprous oxide then remains as an amorphous powder, of a fine red colour (Wöhler and Liebig, Pogg. Ann. xxi. 581).—4. A solution of equal parts of cupric sulphate and sugar, is mixed with a sufficient quantity of soda-ley to dissolve all the copper, and gently heated; cuprous oxide then separates in the form of a crystalline powder (Mitscherlich, J. pr. Chem. xix. 430).—5. A very fine-coloured oxide is obtained by pouring a cold saturated solution of cupric sulphate into an excess of potash-ley; leaving the precipitated cupric hydrate to settle; then, after washing and pressing, diffusing it, while still moist, through 7 times its weight of water in which 3 parts of sugar are dissolved; adding a solution of 2 pts. hydrate of potassium in a quantity of water equal to that which has been used for dissolving the sugar; agitating the mixture strongly; straining it through linen; and heating it over the water-bath, with brisk agitation. Cuprous oxide is then deposited, and, after



being well washed, exhibits a fine red colour.—6. Cuprous oxide may be obtained in small shining cubical crystals, by filling a test-tube with a neutral solution of cupric nitrate, placing a small quantity of cupric oxide at the bottom, introducing a clean strip of copper-plate, closing the tube air-tight, and leaving it to itself for a few months (Becquerel). The oxide is sometimes found in a similar form on the surface of antique bronzes which have been buried in the earth for a long time.

In whatever way cuprous oxide may be prepared, its colour is finer and more approaching to crimson, in proportion as it is purer and more finely divided. The crystals, whether natural or artificial, yield a crimson powder by trituration.

Cuprous oxide is reduced to the metallic state by gentle ignition with charcoal or hydrogen; also by potassium at a temperature a little above the melting point of the latter. It imparts a ruby-red colour to glass-fuses, if fused in such a manner as to avoid oxidation. It dissolves in excess of hydrochloric acid, forming a solution of cuprous chloride, which is decomposed by water. Most other acids, viz. sulphuric, phosphoric, acetic, oxalic, tartaric, and citric acid, decompose it, forming cupric salts and separating metallic copper; nitric acid converts it into cupric nitrate. Hence there are but few cuprous oxygen-salts; indeed the only such salts known are the sulphites, and the double sulphites of cuprous and the alkali-metals, produced by treating cupric solutions with alkaline sulphites (ii. 56). With bromine-water, it yields cupric bromide and cupric oxide.

*Hydrated Cuprous oxide, or Cuprous hydrate,  $4\text{Cu}^{\text{I}}\text{O} \cdot \text{H}^{\text{I}}\text{O}$ ?*—When a solution of cuprous chloride in hydrochloric acid is poured into excess of soda or potash-ley, or when recently precipitated cupric hydrate is boiled for a few minutes with a solution of milk-sugar containing a small quantity of carbonate of sodium, the liquid then diluted with water, and the precipitate washed, cuprous hydrate is obtained as an orange-yellow powder, which oxidises to cupric hydrate, on exposure to the air. It retains its water at  $100^{\circ}\text{C}$ ., but gives it up completely at  $360^{\circ}$ , without change of colour; it does not, indeed, assume the red colour of the anhydrous oxide, prepared by the methods previously described, till it is heated to commencing whiteness.

*Ammonio-cuprous oxide.*—When cuprous oxide or hydrate, or a mixture of cupric oxide and copper-filings, is placed, together with excess of ammonia, in a stoppered bottle, a colourless liquid is obtained, which oxidises so quickly on exposure to the air, that it exhibits a blue colour while being poured in a thin stream from one vessel to another (Bergmann, *Opuscula*, iii. 389; Proust).

*SESQUIOXIDE OF COPPER.* *Cupric acid,  $\text{Cu}^{\text{II}}\text{O}^{\text{II}}$ ?*—Not known in the separate state. Some of its salts have been obtained in the state of solution, by passing chlorine gas into potash or soda-ley in which hydrated cupric oxide is diffused; but they cannot be obtained in the solid state, inasmuch as they are decomposed, with violent evolution of oxygen, soon after their formation. Cuprate of calcium has however been obtained in the form of a beautiful rose-coloured substance, by mixing chloride of lime with a solution of cupric nitrate; it decomposed but slowly (Krüger, *Pogg. Ann.* lxxii. 446). According to Crum (*Ann. Ch. Pharm.* lv. 213), the oxygen-compound of copper contained in this salt is a sesquioxide,  $\text{Cu}^{\text{II}}\text{O}^{\text{II}}$ .

*PEROXIDE OF COPPER.*—1. Formed by agitating the hydrated protoxide with a large excess of very dilute peroxide of hydrogen at a temperature of  $0^{\circ}\text{C}$ .—2. By mixing cupric nitrate with excess of aqueous peroxide of hydrogen, and precipitating the copper at  $0^{\circ}\text{C}$ . by caustic potash added in moderate excess. The resulting peroxide of copper is washed with cold water, pressed between bibulous paper, and dried in vacuo. Yellowish-brown powder (or olive-green, if contaminated with hydrated cupric oxide), tasteless, and without action on vegetable colours. Contains nearly twice as much oxygen as the protoxide. At a temperature short of  $100^{\circ}\text{C}$ ., it gives off oxygen, and is converted into protoxide; in the moist state, it decomposes in the course of 12 hours, even at ordinary temperatures the decomposition being greatly accelerated by the presence of strong caustic potash. It is insoluble in water. With acids, it forms ordinary cupric salts and peroxide of hydrogen (Thénard). It is perhaps not a higher oxide of copper, as Thénard supposes, but rather a compound of cupric oxide with peroxide of hydrogen.

**COPPER, OXYBROMIDE OF.** A solution of cupric bromide, treated with a quantity of ammonia, not sufficient for complete precipitation, yields a hydrated oxybromide, in the form of a pale green powder, which gives off its water when gently heated, and at a higher temperature gives off bromine, and leaves a grey compound of cupric oxide with cuprous bromide. (Löwig.)

Bromine-water forms, with cupric oxide, an insoluble olive-green substance, which is probably a mixture of cupric hypobromite and oxybromide. It liberates nitrogen from ammonia, does not discharge vegetable colours, is decomposed by the weakest

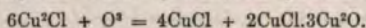
acids, with evolution of bromine, and at 100° C. gives off oxygen, bromine, and water, and is converted into cupric oxybromide. (Balard, J. pr. Chem. iv. 179.)

**COPPER, OXYCHLORIDES OF.** Four of these compounds (cupric oxychlorides) are known both in the anhydrous and hydrated states.

a.  $\text{Cu}^2\text{ClO}$ , or  $\text{CuCl.Cu}^2\text{O}$ . An aqueous solution of cupric chloride, treated with a quantity of potash not sufficient to decompose the whole of it, yields a pale green precipitate, consisting of  $\text{Cu}^2\text{ClO.2H}^2\text{O}$ , which gives off its water when strongly heated, leaving the anhydrous compound in the form of a black powder. This, when moistened with water, is converted into a bright green powder, containing  $2\text{Cu}^2\text{ClO.3H}^2\text{O}$ ; and this last hydrate, heated to 133° C., gives off  $\frac{2}{3}$  of its water, leaving a chocolate-coloured powder, consisting of  $\text{Cu}^2\text{ClO.H}^2\text{O}$ . (Kane, Ann. Ch. Phys. lxxii. 277.)

b.  $\text{Cu}^2\text{Cl}^2\text{O}^3 = 2\text{CuCl.3Cu}^2\text{O}$ . The anhydrous compound, which is obtained by gently heating the hydrate, forms a brown powder; at a red heat, it gives off oxygen, and is converted into a compound of cupric oxide and cuprous chloride:  $2\text{CuCl.3Cu}^2\text{O} = 2(\text{Cu}^2\text{Cl.Cu}^2\text{O}) + \text{O}$ . (Proust.)

This oxychloride occurs in nature, associated with various quantities of water, as *Atacamite* (i. 429). Hydrates are also prepared by the following processes: 1. The anhydrous compound is converted into the hydrate by contact with water. 2. Moist cuprous chloride exposed to the air, is converted into a green mixture of hydrated protochloride, which may be extracted by water, and hydrated cupric oxychloride:



3. By digesting aqueous protochloride of copper with the hydrated protoxide; or by mixing it with a small quantity of alkali, sufficient, however, for the precipitation of the dissolved salt. 4. By exposing copper-foil to the air, moistening it repeatedly with hydrochloric acid or solution of sal-ammoniac, and exhausting the product with water. The artificially prepared salt is a pale green powder. It is prepared, by the last process, on the large scale, and constitutes the pigment called *Brunswick green*, which has the advantage of not being affected by sunlight. When gently heated, it gives off water, and is converted into the black anhydrous compound. Cold sulphuric acid turns it brown, and separates protochloride of copper. When heated, it gives off hydrochloric acid. It is insoluble in water, but easily soluble in acids. (Gm. v. 441.)

c.  $\text{Cu}^2\text{ClO}^2 = \text{CuCl.2Cu}^2\text{O}$ . This compound remains as a green hydrate when the ammonio-chloride,  $\text{NH}^4\text{CuCl}$ , is treated with water. When heated, it gives off its water, and becomes chocolate-brown, and if afterwards exposed to the air, regains a portion of the water which it has lost.

**COPPER, OXYFLUORIDE OF.**  $\text{Cu}^2\text{F}^2\text{O.H}^2\text{O}$ , or  $2\text{CuF.Cu}^2\text{O} + \text{H}^2\text{O}$ .—Pale green insoluble powder, formed by digesting aqueous hydrofluoric acid with excess of cupric carbonate, or by decomposing cupric fluoride (ii. 65), with boiling water. (Berzelius.)

**COPPER, OXYGEN-SALTS OF.** For the general properties of these salts, see ii. 55, 56; for the particular descriptions, see the several ACIDS.

**COPPER OXYSULPHIDES.** The compound  $\text{Cu}^{12}\text{S}^3\text{O}$ , or  $5\text{Cu}^2\text{S.Cu}^2\text{O}$ , is obtained, according to Pelouze, by dropping sulphide of sodium into an ammoniacal solution of a cupric salt, heated to 75°—80° C. till the blue colour just disappears, then quickly collecting and washing the resulting precipitate. If the temperature is allowed to rise during the precipitation to 95°—100° C., an oxysulphide of different composition is obtained, which, if boiled with a cupric salt containing excess of ammonia, decolorises and reduces it to a cuprous salt.

An oxysulphide is likewise formed when sulphide of copper is heated in a solution of a cupric salt, most readily if the solution is alkaline.

The brown substance which forms in the first instance, when copper is heated with oil of vitriol, for the preparation of sulphurous acid, has the composition  $2\text{Cu}^2\text{S.Cu}^2\text{O}$ . By the further action of the acid, which abstracts copper, this compound is converted into  $2\text{Cu}^2\text{S.Cu}^2\text{O}$ ; and when the evolution of gas is at an end, the residual black substance has the composition  $\text{Cu}^2\text{S.Cu}^2\text{O}$ . (Mauméné, Ann. Ch. Phys. [3] xviii. 311; Handw. d. Chem. iv. 735.)

**COPPER, PHOSPHATES OF.** Three cupric phosphates occur as natural minerals, viz.:

Libethenite . . .	$4\text{Cu}^2\text{O.P}^2\text{O}^3 + \text{H}^2\text{O}$ or $\text{Cu}^2\text{PO}^4.\text{CuHO}$ .
Phosphocalcite . .	$6\text{Cu}^2\text{O.P}^2\text{O}^3 + 3\text{H}^2\text{O}$ or $\text{Cu}^2\text{PO}^4.3\text{CuHO}$ .
Thrombolite . . .	$5\text{Cu}^2\text{O.3P}^2\text{O}^3 + 10\text{H}^2\text{O}$ or $\text{Cu}^2\text{PO}^4.2\text{CuPO}^3 + 5\text{H}^2\text{O}$ .

(See these Minerals; also PHOSPHATES.)



**COPPER, PHOSPHIDES OF.** Copper and phosphorus unite readily at high temperatures. By carefully dropping phosphorus on melted copper in a crucible, the metal may be made to take up as much as 11 per cent. of phosphorus. Phosphorus increases the fusibility and hardness of copper, and when present in large quantity, renders it brittle at ordinary temperatures. Copper containing 11 per cent. of phosphorus is extremely hard, and can scarcely be touched by a file. It has a more or less steel-grey colour, and is susceptible of a fine polish, but speedily tarnishes, especially in a London atmosphere. (*Percy's Metallurgy*, i. 279.)

Several definite phosphides of copper have been prepared by H. Rose (Pogg. Ann. iv. 110; xiv. 188; xxiv. 321, 331).

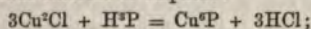
*a. Dicupric Phosphide*,  $\text{Cu}^2\text{P}$ .—Greyish black crystalline substance, obtained by passing hydrogen gas over dicupric phosphate ( $\text{Cu}^2\text{HPO}_4$ ), at a very strong red heat.

A mixture of dicupric phosphide with chlorate of potassium and cuprous sulphide or levigated coke, to increase its conducting power, is used as a fuse for firing charges of gunpowder by magneto-electricity. (Abel, Chem. Soc. J. xiv. 183.)

*b. Tricupric Phosphide*,  $\text{Cu}^3\text{P}$ , is obtained by passing phosphoretted hydrogen gas, ( $\alpha$ ) over heated protochloride of copper,  $3\text{CuCl} + \text{H}^3\text{P} = \text{Cu}^3\text{P} + 3\text{HCl}$ , or ( $\beta$ ) through a solution of cupric sulphate (H. Rose, Pogg. Ann. xiv. 188; xxiv. 321). The first process yields it in the form of a black powder, which, when strongly ignited in a close vessel, is converted into a greyish-black metallic-looking mass, but does not assume the red colour of copper at any temperature. By the second process, it is obtained in black flocks, which, after gentle heating in vacuo, assume a red colour, like that of copper precipitated by zinc (H. Rose). It does not fuse at the melting point of glass, but is more fusible than copper. (Landgrebe, Schw. J. 411, 464.)

Tricupric phosphide  $\alpha$  exhibits a phosphorus-flame on charcoal before the blow-pipe,  $\beta$  does not;  $\alpha$  gives off half its phosphorus when very strongly united in a current of hydrogen gas (H. Rose, Pogg. Ann. iv. 110). Both varieties dissolve readily in nitric acid, with formation of phosphoric acid, especially  $\alpha$ , if not previously heated. Hot strong sulphuric acid dissolves  $\beta$ , with evolution of sulphurous anhydride. If not previously heated,  $\beta$  dissolves in hydrochloric acid more readily than pure copper, with evolution of non-spontaneously inflammable phosphoretted hydrogen (Buff).  $\beta$ , if not previously heated, is permanent in dry air, but when exposed to a moist atmosphere is converted into cupric phosphate. Before the blow-pipe, it burns to a black bead of cupric phosphate, which solidifies to a white enamel on cooling. (Landgrebe.)

*c. Tricuprous Phosphide*,  $\text{Cu}^3\text{P}$ , or  $\text{CuCu}^2\text{P}$ .—Produced by passing phosphoretted hydrogen over cuprous chloride or sulphide:



also by passing hydrogen gas over tricupric phosphide, at a very strong red heat. It is a black powder, or, after strong ignition, a light grey mass, having the metallic lustre. On charcoal, before the blow-pipe, it emits a phosphorus-flame. It is insoluble in hydrochloric acid, but dissolves in nitric acid or aqua regia, forming cupric phosphate. (H. Rose.)

**COPPER, PURPLE.** (See SULPHIDES OF COPPER AND IRON, ii. 80.)

**COPPER, RED.** (See COPPER, OXIDES OF, ii. 70.)

**COPPER, SELENIDES OF.** *Cupric Selenide*,  $\text{Cu}^2\text{Se}$ , is obtained by precipitating cupric sulphate with selenhydric acid, in black flakes, which become dark grey when dry, and acquire metallic lustre by pressure. It gives off half its selenium on distillation. (Berzelius.)

*Cuprous Selenide*,  $\text{Cu}^+\text{Se}$ , or  $\text{CuCu}^+\text{Se}$ . Found native, as *Berzelianite*, at Skrikerum in Sweden, and near Lehrbach in the Hartz, in soft thin dendritic crusts, with silver-white colour and metallic lustre. The same compound is produced by heating copper with selenium, and by igniting cupric selenide in a close vessel. Before the blowpipe it emits the odour of selenium, and fuses to a grey bead of brittle, easily fusible copper, still retaining selenium. (Berzelius.)

*Selenide of Copper and Lead.* (See LEAD, SELENIDE OF.)

**COPPER, SILICATES OF.** The *metasilicate*,  $\text{Cu}^+\text{SiO}_3$ , occurs native with 1 at. water, as *Diopside*, and with 2 at. water, as *Chrysocolla*. Other copper silicates of less definite composition are likewise found. (See SILICATES.)

**COPPER, SILICIDE OF.** Silicon may be melted with copper into a ductile bead before the blow-pipe, and the compound leaves a siliceous skeleton when dissolved in acids (Berzelius). By heating copper to intense whiteness with white sand and charcoal, a compound is obtained perfectly soluble in acids, the solution when evaporated leaving 5 per cent. of silica (Berzelius). Percy, by this process, obtained

a compound containing 1.82 per cent. silicon. It had a specific gravity of 8.70, was malleable while cold, but brittle at a red heat.

A compound containing from 10 to 11 per cent. of silicon is obtained by heating copper foil or filings with siliconfluoride of potassium or sodium, and metallic sodium (Deville). It varies in colour from yellow to greyish white, is very hard and brittle, easily pulverised, more fusible than copper, and is readily attacked by nitric acid, either strong or dilute, with separation of a grey powder: the solution gelatinises on evaporation. (*Percy's Metallurgy*, i. 283.)

**COPPER, SULPHATE OF.** Neutral cupric sulphate,  $\text{Cu}^2\text{SO}_4 + 5\text{H}_2\text{O}$  occurs native as *Cyanosite* (g. v.); a basic sulphate,  $\text{Cu}^2\text{SO}_4 \cdot 6\text{Cu}^2\text{OH}$ , also occurs native as *Brochantite* (i. 664). A sulphato-chloride of copper, called *Connellite*, is found in Cornwall (ii. 11). See also SULPHATES.

**COPPER, SULPHIDES OF.** Copper has a great affinity for sulphur, burning in its vapour, and uniting with it even at ordinary temperatures, when the two substances are triturated together in the finely divided state. There are two well defined sulphides of copper,  $\text{Cu}^2\text{S}$  and  $\text{Cu}^+\text{S}$ , corresponding to the oxides, and four more of less defined constitution, but supposed to contain respectively 2, 3, 4, and 5 at. sulphur to 2 at. copper.

**PROTOSULPHIDE OF COPPER, OR CUPRIC SULPHIDE,  $\text{Cu}^2\text{S}$  or  $\text{CuS}$ .** This compound is found native, as *Covellin*, *Indigo copper*, *Blue copper*, or *Breithauptite*, sometimes in hexagonal plates, with very perfect basal cleavage, more commonly massive or spheroidal, crystalline on the surface. It is soft, flexible in thin leaves, of specific gravity 3.8, opaque, of bluish-black colour, with faint resinous lustre. It occurs, with other copper ores, at Leogang in Salzburg, Keiles in Poland, Langerhausen in Saxony, Mansfeld in Thuringia, and in the fumaroles of Vesuvius, where it forms a sooty deposit or black network, like a spider's web. (Gm. v. 422; Dana, ii. 65.)

Cupric sulphide is thrown down from cupric salts by sulphydric acid or sulphide of ammonium, as a brown precipitate, which becomes brown-black when collected, and greenish-black on drying; it oxidises very quickly on exposure to the air, acquiring an acid reaction, and, if moist, is completely converted into cupric sulphate (ii. 57). It is likewise produced by triturating cuprous sulphide with cold strong nitric acid, which abstracts half the copper.

When cupric sulphide is treated with hot nitric acid, the copper is oxidised, part of the sulphur is converted into sulphuric acid, and the rest is separated, so that the resulting solution contains both nitrate and sulphate of copper. Hot concentrated *hydrochloric acid* slowly converts it into cupric chloride, with evolution of sulphydric acid, and separation of sulphur; this reaction takes place most easily with the recently precipitated sulphide. Cupric sulphide decomposes *silver-salts*, the copper dissolving, and sulphide of silver being precipitated. It is insoluble in aqueous sulphurous acid, potash, and the fixed alkaline sulphides, slightly soluble in sulphide of ammonium.

**HEMISULPHIDE OF COPPER, OR CUPROUS SULPHIDE,  $\text{Cu}^+\text{S} = \text{Cu}_2\text{S}$ , or  $\text{Cu}_2^+\text{S}$ ,** also called *Disulphide of copper*.—Found native, as *Copper-glance*, *Vitreous copper*, or *Redruthite*, in crystals of the trimetric system, with the form of six-sided prisms,  $\infty P : \infty \bar{P} :: \infty P$ . Ratio of brachydiagonal, macrodiagonal and principal axis, = 0.5822 : 1 : 0.9741.  $\infty P : \infty \bar{P} = 60^\circ 25'$ . Cleavage very imperfect, parallel to  $\infty P$  (Kopp). Twin crystals are of frequent occurrence. It also occurs massive, with granular or compact and impalpable structure. Specific gravity = 5.5—5.8. Hardness = 2.5—3. Colour blackish lead-grey; lustre metallic; streak lead-grey, sometimes shining. Fracture conchoidal. Sectile. Fine crystals of this mineral are found in the Cornish mines; it occurs also in Haddingtonshire, Ayrshire, and Fair Island, Scotland. The compact and massive varieties occur in Siberia, Hesse, Saxony, the Bannat; also in Connecticut, New Jersey, and other parts of the United States; large and brilliant crystals are found at Bristol, Connecticut. Copper pyrites, purple copper, and black copper, occur as pseudomorphs after copper-glance. (Dana, ii. 46.)

Cuprous sulphide is prepared: 1. By triturating copper with sulphur. When 64 pts. (2 at.) of finely divided copper, obtained by reducing the carbonate with hydrogen, and 16 pts. ( $\frac{1}{2}$  at.) of milk of sulphur are dried together over oil of vitriol, and triturated together in a mortar, so gently that no heat is produced by the friction, they combine as soon as a uniform mixture is attained, and form bluish cuprous sulphide, the combination being attended with a development of heat which raises the mass to redness. If the proportion of the copper to the sulphur be even slightly altered, the experiment fails, even though the mortar be warmed. If the mortar be warmed to  $20^\circ$  to  $25^\circ \text{C}$ , it is not necessary to dry the powders previously, and moreover, flowers of sulphur may be used instead of milk of sulphur, only that longer trituration is neces-



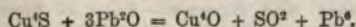
sary to induce combination (Winkelblech, Ann. Ch. Pharm. xxi. 34). Sulphide of copper is also formed by triturating copper filings with sulphur and water.—2. Thin copper leaf burns with vivid inflammation in a glass flask in which sulphur has been heated till it volatilises. 8 pts. of copper filings mixed with 3 pts. of pounded sulphur unite, with incandescence, when heated. The same compound is obtained by fusing together plates of copper and pounded sulphur, arranged in a crucible in alternate layers.—3. By igniting protoxide of copper with sulphur.—4. 100 pts. of dry cupric sulphate heated to whiteness in a crucible lined with charcoal, yield 47.6 pts. of cuprous sulphide, mixed with a few granules of the metal. (Berthier, Ann. Ch. Phys. xxii. 236.)

Artificial cuprous sulphide has a density of 5.9775 (Karsten); it is of a blackish lead-grey colour, and fuses much more easily than the metal.

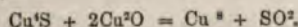
Cuprous sulphide is not decomposed when heated to redness out of contact of air; but if the air has access to it, combustion takes place, and sulphurous anhydride and free cupric oxide are produced. When heated to redness in a current of aqueous vapour, it is but slightly decomposed; but at a white heat, it yields large quantities of hydrogen gas and sulphuretted hydrogen, together with sublimed sulphur, and the copper is completely reduced to the metallic state (Regnault, Ann. Ch. Phys. lxii. 378). [There is no statement as to what becomes of the oxygen of the water.] By phosphoretted hydrogen gas at a red heat, it is very slowly resolved into  $\text{Cu}^2\text{P}$  and sulphuretted hydrogen (H. Rose):



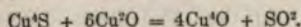
It is not altered by ignition in a stream of hydrogen (H. Rose). It is not decomposed by chlorine gas at ordinary temperatures, very slowly when heated (H. Rose, Pogg. Ann. xlii. 540). It dissolves with difficulty in strong boiling hydrochloric acid, with evolution of sulphuretted hydrogen and formation of hydrochloric acid and cuprous oxide; in heated nitric acid, it dissolves with separation of sulphur, whereas cold nitric acid withdraws half the copper and leaves protosulphide of copper. 100 pts. of cuprous sulphide, ignited with 77 pts. or rather less of nitre, yield from 66 to 70 pts. of metallic copper (Berthier). When cuprous sulphide is fused with a mixture of caustic soda and carbonate of sodium, part of the copper is reduced. The same reducing action is exerted by a mixture of carbonate of sodium and charcoal, whereas carbonate of sodium or potash alone has no effect. When 100 pts. of cuprous sulphide are fused with 70 pts. of dry carbonate of sodium and with charcoal, one half of the copper is reduced, and the rest combines as sulphide of copper with the sulphide of sodium which is formed. When 1 pt. of cuprous sulphide is heated to whiteness with 4 pts. of carbonate of sodium, in a crucible lined with charcoal, nearly all the copper is reduced. 100 pts. of cuprous sulphide ignited with 400 pts. of dry carbonate of sodium and 30 or 40 pts. of iron, yield at most 60 pts. of copper. Also, when cuprous sulphide is heated to whiteness with baryta or lime and charcoal, part of the copper is reduced, and sulphide of copper and barium or calcium formed at the same time (Berthier, Ann. Ch. Phys. xxxiii. 160). When cuprous sulphide is fused with protoxide of lead, the mass boils up and yields sulphurous anhydride, cuprous oxide, which combines with the undecomposed lead-oxide, forming a red shining slag, and metallic lead; 100 pts. of cuprous sulphide and 200 litharge, yield 104 pts. of copper containing lead. With from 300 to 500 pts. of litharge, a grey, semiductile alloy, rich in lead, is obtained. When 1000 pts. of litharge are used, 280 pts. of ductile lead separate out, and 2500 pts. of litharge yield 385 pts. of lead. It is only therefore with this last proportion that the whole of the sulphide of copper is resolved into sulphurous anhydride and cuprous oxide:



Accordingly, 160 pts. (1 at.)  $\text{Cu}^2\text{S}$  should separate 624 pts. (6 at.) of lead = 100 : 390 (Berthier, Ann. Ch. Phys. lxxxix. 246). Metallic lead exerts no decomposing action on cuprous sulphide when fused with it (Karsten). Cuprous sulphide, ignited with cupric oxide is easily converted into sulphurous anhydride and metallic copper, or cuprous oxide. 1 at.  $\text{Cu}^2\text{S}$  and 2 at.  $\text{Cu}^2\text{O}$  are completely converted into sulphurous anhydride and copper:



With 6 at.  $\text{Cu}^2\text{O}$ , the only products are sulphurous anhydride and cuprous oxide:



Any excess of cuprous sulphide remains undecomposed. Metallic iron decomposes cuprous sulphide, though very imperfectly, yielding copper containing iron, iron

containing copper, and sulphide of copper and iron. *Ferric oxide* exerts but a slight decomposing action, and ferrous silicate none at all. (Gm. v. 421.)

*Polysulphides of copper.*—An aqueous solution of pentasulphide of potassium forms, with cupric salts, a liver-coloured precipitate, consisting of  $\text{Cu}_2\text{S}_5$ , which turns black after drying, is not altered by exposure to the air, or by washing with boiling water, and when recently precipitated dissolves in aqueous carbonate of potassium, forming a brown solution.—The disulphide, trisulphide, and tetrasulphide of potassium, form with cupric salts, precipitates of the same colour, likewise soluble in carbonate of potassium, and consisting either of the compounds,  $\text{Cu}_2\text{S}_2$ ,  $\text{Cu}_2\text{S}_3$ , and  $\text{Cu}_2\text{S}_4$ , or of mixtures of  $\text{Cu}_2\text{S}$  and  $\text{Cu}_2\text{S}_2$ . (Berzelius.)

**Sulphides of Copper and Antimony.** *a. Wolfsbergite. Antimonial Copper, Chalcostibites, Kupferantimonglanz.*—A mineral occurring at Wolfsberg in the Harz, and at Guadiz in Spain, in small aggregated tabular prisms of the trimetric system, exhibiting the faces  $\text{oP} \propto \text{P} \propto \text{P}2 \propto \text{P}\infty$ . Inclination of faces  $\infty \text{P} : \infty \text{P} = 101^\circ$ ;  $\infty \text{P}2 : \infty \text{P}2 = 138^\circ 12'$ ;  $\infty \text{P}2 : \infty \text{P}\infty = 112^\circ 24'$ . Cleavage very distinct, parallel to  $\infty \text{P}\infty$ ; less distinct, parallel to  $\text{oP}$ . Specific gravity 4.748. Hardness = 3–4. Lustre metallic. Streak black. Colour between lead- and iron-grey. Opaque. Fracture conchoidal. Before the blowpipe it decrepitates, fuses readily, and on charcoal gives fumes of antimony; after strong heating with soda, it yields a globule of copper.

The mineral is a cuprous sulphantimonite,  $\text{Cu}_2\text{S.Sb}_2\text{S}_3$ , or  $\left\{ \begin{smallmatrix} \text{Cu}' \\ \text{Sb}'' \end{smallmatrix} \right\} \text{S}_2$ .

	Calculation.		H. Rose. Wolfsberg.	Th. Richter. Guadiz.
	63.3	25.61		
Cu <sup>2</sup>	. . . . .	120.3	46.81	48.30
Sb	. . . . .	64.0	26.34	25.29
S <sup>2</sup>	. . . . .	. . . . .	1.39	1.23
Iron	. . . . .	. . . . .	0.56	
Lead	. . . . .	. . . . .		
	247.6	100.00	99.56	100.18

*b. Wolchite. Antimonial Copper-glance, Antimonkupferglanz.*—A mineral occurring in the iron mines at St. Gertraud, Carinthia, in short rhombic prisms, cleaving imperfectly parallel to the brachydiagonal; also massive. Specific gravity 5.7–5.94. Hardness = 3. Fracture conchoidal to uneven. Brittle.

The analyses of this mineral differ widely, as the following table will show:—

	Schröter.	Rammelsberg.
	28.60	16.81
Sulphur	. . . . .	15.23
Copper	. . . . .	42.83
Antimony	. . . . .	43.69
Arsenic	. . . . .	24.41
Lead	. . . . .	24.46
Iron	. . . . .	6.03
	29.90	15.59
	1.40	16.15
	99.93	0.36
		100.11

The mineral is probably nothing but a partially altered Bournonite (i. 651). (Rammelsberg, p. 80; Dana, ii. 82.)

For the *Sulphantimonites of copper and iron*, &c., see TETRAHEDRITE.

**Sulphides of Copper and Arsenic.**—None of these compounds occur as natural minerals (see SULPHARSENITES and SULPHARSENATES, i. 390, 393). In many varieties of grey copper the antimony is partly replaced by arsenic. (See TENNANTITE.)

**Sulphides of Copper and Bismuth.** *a. Tannenite, Kupferwismuthglanz.*—Occurs at Tannenbaum, near Schwarzenberg in the Erzgebirg, in thin striated prisms, apparently trimetric. Lustre bright metallic. Colour greyish to tin-white. Heated in an open tube it yields sulphur. Before the blowpipe on charcoal, it fuses easily with intumescence, and yields with soda a globule of copper. Dissolves in nitric acid with deep bluish-green colour.

Schneider found in this mineral (mean of two analyses) 18.83 per cent. S, 62.16 Bi, and 18.72 Cu, which agrees very nearly with the formula  $\text{Cu}_2\text{S.Bi}_2\text{S}_3$ , or  $\left\{ \begin{smallmatrix} \text{Cu}' \\ \text{Bi}'' \end{smallmatrix} \right\} \text{S}_2$  (calculation 19.08 S, 62.01 Bi, 18.91 Cu). The mineral is, therefore, analogous in constitution to Wolfsbergite. (Rammelsberg, p. 103; Dana, ii. 73.)

*b. Wittichenite. Cupreous Bismuth, Kupferwismuthers.*—A mineral found in the cobalt mines near Wittichen, in Baden, sometimes massive and disseminated, some-



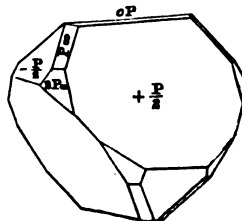
times in coarse columnar shapes, or aggregates of imperfect prisms (trimetric?), cleaving in one direction. Specific gravity = 5. Hardness = 3.5. Colour steel-grey or tin-white, tarnishing pale lead-grey. Streak black. Fuses easily in an open tube, yielding sulphur and a white sublimate. On charcoal before the blowpipe it decrepitates, melts, forms a yellow deposit, and after reduction with soda a globule of copper. Boiled with hydrochloric acid in a flask, without access of air, it dissolves, with elimination of sulphuretted hydrogen, to a nearly colourless liquid, a certain quantity of admixed metallic bismuth remaining undissolved. If, on the other hand, the air has access to the liquid, the metallic bismuth likewise dissolves after a while. Nitric acid dissolves the mineral with separation of sulphur.

The analysis of this mineral by Schneider (Pogg. Ann. xciii. 305, 472), after deduction of the admixed metallic bismuth, gives 19.42 per cent. S, 43.05 Bi, and 37.53 Cu, agreeing with the formula  $3\text{Cu}^2\text{S} \cdot \text{Bi}_2\text{S}_3$ , or  $\frac{\text{Cu}^2}{\text{Bi}^3} \left\{ \text{S}^2 \right\}$  (calculation 19.50 S, 42.98 Bi, and 38.42 Cu). Other analysts have obtained different results, because they overlooked the admixed metallic bismuth (Rammelsberg, p. 104). A grey massive mineral found in the Geistergang at Joachimsthal, containing 9.94 per cent. S, 30.74 As, 45.31 Bi, and 13.04 Cu, appears to be a mixture. (Rammelsberg, *loc. cit.*)

*Sulphides of Copper, Bismuth, and Lead.* See NEEDLE-ORE.

**Sulphides of Copper and Iron.** *a. Copper Pyrites. Chalcopyrite, Towanite, Cuivre pyriteux, Kupferkies.*  $\text{CuFeS}_2$ , or  $\text{Cu}^2\text{S} \cdot \text{Fe}^2\text{S}_2$ .—This mineral occurs in crystals of the dimetric system, often tetrahedral. The primary form P, for which the length of the principal axis is to that of the secondary axis as 0.985 : 1, the angle of the terminal edges =  $109^\circ 53'$ , and of the lateral edges =  $108^\circ 40'$ , occurs in the hemihedral form as a sphenoid (see CRYSTALLOGRAPHY), both alone and in combination, as in *fig. 145*. Cleavage parallel to  $2P\infty$ , but generally indistinct. Frequently in twins. It often occurs also massive and impalpable. Specific gravity 4.1–4.3. Lustre metallic. Colour brass-yellow, subject to tarnish, and often iridescent. Streak greenish-black, a little shining, opaque. Fracture conchoidal, uneven. Rather sectile. It decrepitates when heated, acquiring a darker colour, and sometimes giving off a trace of sulphur. Gives off sulphurous anhydride when roasted. On charcoal before the blowpipe it melts, with intumescence and sparkling, to a globule which is dark grey within, black and rough without, and is attracted by the magnet. The roasted globule gives, with fluxes, the reactions of copper and iron. It dissolves in nitric acid, with separation of sulphur.

*Fig. 145.*



*Analyses.*—*a.* From Ramberg in the Sayn district, crystallised (H. Rose).—*b.* From the Fürstenberg district, crystallised (H. Rose).—*c.* From Ormijärvi, Finland (Hartwall).—*d.* English;  $\alpha$  crystallised,  $\beta$  botryoidal.—*e.* Allevard, Département de l'Isère, massive (Berthier).—*f.* From Kaafjord, Norway (Malaguti and Durocher).—*g.* Val Castrucci, Tuscany.—*h.* Monte Catini, Tuscany. (Bechi.)

	<i>d</i>								
	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>β</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>
Sulphur	35.87	36.52	36.33	35.16	34.46	36.3	38.76	35.62	36.16
Copper .	34.40	33.12	32.20	30.00	31.20	32.1	32.73	34.09	32.79
Iron	30.47	30.00	30.03	32.20	30.80	31.5	28.51	30.29	29.75
Quartz .	0.27	0.39	2.23	2.64	1.10	.	.	.	0.86
	101.01	100.03	100.79	100.00	97.56	99.9	100.00	100.00	99.66

The formula  $\text{CuFeS}_2$  requires 34.59 per cent. Cu, 30.52 Fe, and 34.89 S.

Copper pyrites is the principal copper ore in the Cornish mines, where it occurs associated with tin, purple copper, copper glance, galena, grey copper, and blende. The Cornish copper pyrites is not, however, a rich ore, rarely yielding 12 per cent., generally only 7 or 8, and sometimes only 3 or 4 per cent. of copper. If of a fine yellow colour and yielding readily to the hammer, it may be considered a good ore; but if hard and pale yellow, it is poor, from admixture of iron pyrites. The copper beds of Fahlun in Sweden are also composed chiefly of copper pyrites, which occurs there in large masses, surrounded by a coating of serpentine and imbedded in gneiss. It occurs also at Rammelsberg, near Goslar in the Harz; at Freiberg, in the Bannat; in Hungary; in Thuringia; in Scotland, in Kirkcudbright, Wigtonshire, Perthshire, and Invernesshire; in Tuscany; South Australia; and at numerous localities in the United States.

Copper pyrites is distinguished from iron pyrites, which it somewhat resembles, by

its inferior hardness; it may be cut with the knife, while iron pyrites strikes fire with steel. It differs from gold in being brittle and attacked by nitric acid.

Copper pyrites changes to cupric sulphate on exposure to moisture, especially if heated; it is sometimes also altered to malachite, covellin, chrysocolla, black copper, copper-glance, and oxide of iron.

*b. Purple Copper. Erubescite, Variegated Copper, Liver-coloured Copper Ore, Phillipsite, Bornite (Buntkupfererz, Bunter Kupferkies, Cuivre pyriteux hépatique).—*This mineral forms crystals belonging to the monometric or regular system, namely, the cube, octahedron, rhombic dodecahedron, and intermediate forms. Cleavage octahedral, indistinct. Twin crystals are of frequent occurrence; also imperfect crystallisations, with granular strongly connected structure. Specific gravity = 4.4–5.003. Hardness = 3. Lustre metallic. Colour between copper-red and pinchbeck-brown, quickly acquiring a parti-coloured tarnish. Streak pale greyish black, slightly shining. Fracture small conchoidal, uneven. Brittle.

Purple copper does not give off sulphur when ignited in a test-tube, but when heated in a tube open at both ends, it yields a large quantity of sulphurous anhydride, but no sublimate. Heated on charcoal before the blowpipe, it acquires a dark tarnish, then becomes black, and red on cooling. At a somewhat stronger heat, it melts to a brittle globule, which becomes magnetic after sufficient blowing, and appears greyish-red on the fractured surface. When roasted for a considerable time, and then treated with a small quantity of borax, it yields a button of copper, and if fused with carbonate of sodium after the sulphur is completely expelled, it yields separate granules of copper and iron. After roasting, it exhibits with fluxes the reactions of cupric and ferric oxides. When moistened with hydrochloric acid, it colours the blowpipe flame blue.

There are several varieties of purple copper. Rammelsberg (*Mineralchemie*, p. 114) arranges them in three groups, containing respectively from 56 to 58 per cent., 60 to 64 per cent., and 70 per cent. copper.

1. Purple copper, containing from 56 to 58 per cent. copper.—*a.* Crystallised, from the Condurra mine near Cambern, Cornwall. *b.* Crystallised, from Redruth, in Cornwall (Chadnew). *c.* Crystallised, of unknown origin (Varrentrapp). *d.* Massive, from Monte Cattini in Tuscany (Bechi). *e.* Massive, from the Märtensberg mine, Dalarne, Sweden. (Plattner.)

	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>	<i>e.</i>
Sulphur . . .	28.24	26.84	26.98	24.92	25.80
Copper . . .	56.76	57.89	58.20	55.88	56.10
Iron . . .	14.84	14.94	14.84	18.03	17.36
	99.84	99.67	100.02	98.83	99.26

2. Containing from 60 to 64 per cent. copper.—*f.* From Ferruccio in Tuscany (Bechi). *g.* From Miemo in Tuscany (Bechi). *h.* From Coquimbo in Chili (Böcking). *i.* From Ross Island, Killarney (Phillips). *j.* From St. Pancrace, Département de l'Aude (Berthier). *k.* From Bristol, Connecticut (Bodemann). *l.* From the Wortzkisch mine, on the White Sea (Plattner). *m.* From Vestanforss Kirchspiel, Westmanland, Sweden (Hisinger). *n.* From Siberia. (R. Brandes.)

	<i>f.</i>	<i>g.</i>	<i>h.</i>	<i>i.</i>	<i>j.</i>	<i>k.</i>	<i>l.</i>	<i>m.</i>	<i>n.</i>
Sulphur	24.70	23.98	25.46	23.75	24.0	25.70	25.06	24.69	22.44
Copper .	60.01	60.16	60.80	61.07	62.3	62.70	63.03	63.33	63.86
Iron .	15.89	15.09	13.67	14.00	13.7	11.53	11.56	11.80	13.21
	100.60	99.23	99.93	98.82	100.0	99.93	99.65	99.82	99.51

3. Containing 70 per cent. copper.—*o.* From Eisleben (Plattner). *p.* From Monte Castelli, Tuscany. *q.* From Nadaud, France (Berthier). *r.* From Sangershausen, near Eisleben. (Plattner.)

	<i>o.</i>	<i>p.</i>	<i>q.</i>	<i>r.</i>
Sulphur . . .	22.65	22.3	20.0	22.58
Copper . . .	69.72	70.0	70.0	71.00
Iron . . .	7.54	7.0	7.9	6.41
	99.91	99.3	97.9	99.99

Rammelsberg regards the several varieties of purple copper as isomorphous mixtures of the compounds  $3\text{Cu}^{\text{S}}.\text{Fe}^{\text{S}}.\text{S}^{\text{S}}$ , and  $n\text{Cu}^{\text{S}}.\text{Fe}^{\text{S}}.\text{S}^{\text{S}}$ . If  $n = 0$ , this formula is reduced to  $3\text{Cu}^{\text{S}}.\text{Fe}^{\text{S}}.\text{S}^{\text{S}}$ , which requires 28.04 per cent. S, 55.60 Cu, and 16.36 Fe, agreeing nearly with analysis *a* of the mineral from the Condurra mine. Any value of  $n$  greater than 2 increases the proportion of copper;  $n = 3$  gives 25.67 per cent. S, 60.85 Cu and 13.48 Fe, which is very nearly the composition of the minerals *h*, *i*, *j*; and  $n = 11$  requires 22.62 per cent. S, 70.40 Cu, and 6.68 Fe, which is nearly the composition of the specimens *o*, *r*.



Purple copper occurs associated with other copper ores. Crystalline varieties are found in Cornwall, mostly in the mines of Tincroft and Dolwath, near Redruth, where it is called by the miners "horse-flesh ore." Massive varieties are found in Ross Island, Killarney, in the cupriferous shale of the Mansfeld district, also in Norway, Siberia, Silesia, the Bannat, and in Pennsylvania, New Jersey, and Connecticut.

*c. Cuban.* This mineral, found at Barracanao in Cuba, is also monometric, occurring in cubes; also massive. Colour between bronze and brass-yellow. Streak, dark, reddish, bronze, black. Specific gravity = 4.026 (Breithaupt); 4.169 (Booth). Hardness = 4. Melts easily before the blow-pipe, giving off fumes of sulphur. The following analyses have been made of it (deducting silica):

	Scheidthauer.	Eastwick.	Stevens.	Magee.
Sulphur . . . . .	34.78	39.93	40.11	40.19
Copper . . . . .	22.96	20.26	21.46	20.71
Iron . . . . .	42.51	38.90	39.55	39.41
	100.25	99.09	101.12	100.31

The first analysis agrees nearly with the formula  $\text{Cu}^2\text{Fe}^2\text{S}^4$ , or  $\frac{\text{Cu}^2\text{S}}{2\text{Fe}^2\text{S}}\text{Fe}^2\text{S}^2$ , which requires 35.38 per cent. S, 23.38 Cu, and 41.24 Fe; the others, which contain a much larger quantity of sulphur, approach more nearly to the formula  $\text{Cu}^2\text{S}.\text{Fe}^2\text{S}^2$ , which requires 42.21 S, 20.84 Cu, and 36.94 Fe. (Rammelsberg, p. 118, Dana ii. 681.)

*d. Copper regulus.* It has already been mentioned that the reguli produced in copper-smelting consist essentially of cuprous sulphide,  $\text{Cu}^2\text{S}$ , associated with sulphides of iron (ii. 27—31 and 34, 36). Field (Chem. Soc. J. xv. 125) regards all copper reguli as compounds of cuprous sulphide in various proportions with 1 at.  $\text{Fe}^2\text{S}^2$ , 1 at.  $\text{Fe}^2\text{S}$ , and 2 at.  $\text{Fe}^2\text{S}$ . The following table exhibits the composition of some samples of furnace reguli at different stages of the smelting process, as compared with this theoretical view. The first is clean regulus from a furnace; the second is the same after some hours roasting; the third the same after further roasting and skimming. The fifth (with 8 at.  $\text{Cu}^2\text{S}$ ) is a specimen of native blue sulphide.

Composition of Copper Regulus.

	With 3 at. $\text{Cu}^2\text{S}$ .		With 5 at. $\text{Cu}^2\text{S}$ .		With 6 at. $\text{Cu}^2\text{S}$ .		With 7 at. $\text{Cu}^2\text{S}$ .		With 8 at. $\text{Cu}^2\text{S}$ .		With 12 at. $\text{Cu}^2\text{S}$ .	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
Sulphur . . . . .	27.06	27.06	25.43	25.27	24.26	24.25	24.41	24.32	24.03	24.12	23.00	22.90
Copper . . . . .	36.09	36.12	46.24	49.34	49.74	49.71	52.37	52.48	54.93	54.21	61.24	61.34
Iron . . . . .	36.84	36.78	28.32	28.19	25.38	25.34	23.00	22.89	21.02	21.13	15.65	15.61

**COPPER, TELLURIDE OF.** Pale red compound. (Berzelius.)

**COPPER, TUNGSTATE OF.** Found native in a mine in Carrabas County, North Carolina. (Dana, ii. 502.)

**COPPER, VANADATE OF.** Occurs native, as Volborthite, in Siberia and Thuringia. *Vanadates of copper and lead* are found in the Lake Superior region, and in Chile. (See VANADATES.)

**COPPER, VARIEGATED.** Syn. with PURPLE COPPER (ii. 77).

**COPPER, VITREOUS.** Syn. with COPPER-GLANCE (ii. 74).

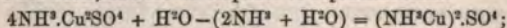
**COPPER-BASES, AMMONIACAL.** The ammonio-chlorides, iodides, oxides, &c., of copper already described, and likewise certain ammonio-copper compounds containing sulphuric and other oxygen-acids, may be regarded as salts of ammonium-molecules, in which the hydrogen is more or less replaced by ammonium and by cupricum, or cuprosium, thus [ $\text{Am} = \text{NH}^4$ ]:

1. Chloride of Cuprammonium }  $\text{NH}^4.\text{CuCl}$  =  $(\text{NH}^4\text{Cu}).\text{Cl}$   
(ii. 53) . . . . .
2. Sulphate of Cuprammonium }  $2\text{NH}^4.\text{Cu}^2\text{SO}^4$  =  $(\text{NH}^4\text{Cu})^2\text{O}^2$   
 . . . . .  $(\text{SO}^2)^2$
3. Sulphate of Cupricum and }  $\text{NH}^4.\text{Cu}^2\text{SO}^4$  =  $\text{NH}^4\text{Cu}$   
 Cuprammonium . . . . .  $\text{Cu}.\text{O}^2$   
 . . . . .  $(\text{SO}^2)^2$
4. Chloride of Ammo-cupram- }  $2\text{NH}^4.\text{CuCl}$  =  $\text{N}(\text{H}^2\text{CuAm}).\text{Cl}$   
 monium . . . . .

5. Iodide of Ammo-cuprammonium . . . . .	$2\text{NH}^3.\text{CuI}$	$= \text{N}(\text{H}^2\text{CuAm})\text{I}$
6. Bromate of Ammo-cuprammonium . . . . .	$2\text{NH}^3.\text{CuBrO}^3$	$= \text{N}(\text{H}^2\text{CuAm})\left\{ \begin{smallmatrix} \text{O} \\ (\text{BrO}^2) \end{smallmatrix} \right\}$
7. Nitrate of Ammo-cuprammonium . . . . .	$2\text{NH}^3.\text{CuNO}^3$	$= \text{N}(\text{H}^2\text{CuAm})\left\{ \begin{smallmatrix} \text{O} \\ (\text{NO}^2) \end{smallmatrix} \right\}$
8. Hydrate of Ammo-cuprammonium . . . . .	$4\text{NH}^3.\text{Cu}^2\text{O} + 4\text{H}^2\text{O}$	$= 2\left\{ \begin{smallmatrix} \text{N}(\text{H}^2\text{CuAm}) \\ \text{H} \end{smallmatrix} \right\} \text{O} + 3 \text{ aq.}$
9. Hyposulphate of Ammo-cuprammonium . . . . .	$4\text{NH}^3.\text{Cu}^2\text{S}^2\text{O}^4$	$= \left[ \begin{smallmatrix} \text{N}(\text{H}^2\text{CuAm}) \\ (\text{S}^2\text{O}^4) \end{smallmatrix} \right] \text{O}^2$
10. Iodide of Ammo-cuprosammonium . . . . .	$2\text{NH}^3.\text{Cu}^2\text{I}$	$= \text{N}(\text{H}^2\text{CuAm})\text{I}$
11. Hydrate of Ammo-tricuprammonium . . . . .	$4\text{NH}^3.3\text{Cu}^2\text{O} + 6\text{H}^2\text{O}$	$= 2\left\{ \begin{smallmatrix} \text{N}(\text{Cu}^2\text{Am}) \\ \text{H} \end{smallmatrix} \right\} \text{O} + 7 \text{ aq.}$
12. Chloride of Diammo-cuprammonium (ii. 53) . . . . .	$3\text{NH}^3.\text{CuCl}$	$= \text{N}(\text{HCuAm}^2).\text{Cl}$
13. Sulphate of Cupricum and Triammo-cuprammonium	$4\text{NH}^3.\text{Cu}^2\text{SO}^4 + \text{H}^2\text{O}$	$= \begin{smallmatrix} \text{N}(\text{CuAm}^2) \\ \text{Cu} \end{smallmatrix} \left\{ \begin{smallmatrix} \text{O}^2 \\ (\text{SO}^2) \end{smallmatrix} \right\} + \text{aq.}$
14. Bromide of Ammo-dicupro-diammonium (ii. 52)	$3\text{NH}^3.2\text{CuBr}$	$= [\text{N}^2(\text{H}^2\text{Cu}^2\text{Am})]''.\text{Br}^2$
15. Bromide of Triammo-dicupro-diammonium (ii. 52)	$5\text{NH}^3.2\text{CuBr}$	$= [\text{N}^2(\text{H}^2\text{Cu}^2\text{Am}^2)]''.\text{Br}^2$
16. Sulphate of Triammo-dicupro-diammonium . . . . .	$5\text{NH}^3.\text{Cu}^2\text{SO}^4$	$= [\text{N}^2(\text{H}^2\text{Cu}^2\text{Am}^2)]'' \left\{ \begin{smallmatrix} \text{O}^2 \\ (\text{SO}^2) \end{smallmatrix} \right\}$

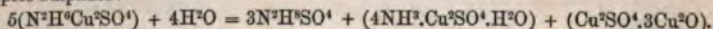
*Pentammonio-cupric Sulphate*, or *Sulphate of Triammo-dicupro-diammonium*,  $5\text{NH}^3.\text{Cu}^2\text{SO}^4$ , is produced when anhydrous cupric sulphate is exposed to the action of dry ammonia-gas, rapid absorption then taking place, attended with rise of temperature and tumefaction. The product is a blue powder, which melts at a moderate red heat, giving off a large quantity of ammonia, together with water and sulphate of ammonium, and leaving cupric sulphate mixed with metallic copper. It dissolves completely in water, forming an azure-blue solution. (Rammelsberg, Pogg. Ann. xx. 150.)

*Tetrammonio-cupric Sulphate*, or *Sulphate of Cupricum and Triammo-cuprammonium*,  $4\text{NH}^3.\text{Cu}^2\text{SO}^4 + \text{H}^2\text{O}$ , also called *Cuprosulphate of ammonia*, *Cuprum ammoniacale*, *Kupfersalmiak*, is produced by treating crystallised cupric sulphate, either pulverised or dissolved in water, with ammonia, till the precipitate is completely redissolved. It crystallises by evaporation, or better, on carefully covering the solution with a layer of alcohol, or exposing it to a low temperature, in long thin prismatic crystals of the trimetric system, transparent, and of dark azure-blue colour. On agitating the ammoniacal solution with alcohol, the salt is precipitated in the form of a blue crystalline powder. It must be quickly dried between bibulous paper, and kept in well closed vessels. It dissolves in  $1\frac{1}{2}$  times its weight of cold water. When exposed to the air, it gives off ammonia and leaves a green powder, which appears to be a mixture of sulphate of ammonium and tetrabasic cupric sulphate,  $\text{Cu}^2\text{SO}^4.3\text{Cu}^2\text{O}$ . When heated for some time to a temperature not exceeding  $149^\circ\text{C}$ , it gives off 2 at. ammonia and 1 at. water, and leaves sulphate of cuprammonium:



and this residue gradually heated to  $205^\circ\text{C}$ . gives off another atom of ammonia, leaving sulphate of cupricum and cuprammonium,  $(\text{NH}^2\text{Cu}).\text{Cu}.\text{SO}^4$ : and this again, if gradually heated to  $260^\circ\text{C}$ . still gives off 1 at. ammonia, and leaves neutral sulphate of copper,  $\text{Cu}^2\text{SO}^4$ . The aqueous solution of the tetrammonio-cupric salt when exposed to the air, deposits tetrabasic cupric sulphate, which is likewise precipitated when the solution is largely diluted with water. Zinc quickly precipitates metallic copper from the solution; cadmium and lead decompose it more slowly; arsenic decomposes it completely, forming cupric arsenite; bismuth, antimony, tin, and iron have no effect upon it. (Gm. v. 449.)

*Neutral Sulphate of Cuprammonium*,  $(\text{NH}^2\text{Cu})^2.\text{SO}^4$ , obtained as above stated by gradually heating the preceding salt to  $149^\circ\text{C}$ . is an apple-green powder, which, on exposure to the air, absorbs water and turns blue. If moistened with a small quantity of water, it becomes very hot, and turns blue immediately. An excess of water decomposes it into sulphate of ammonium, tetrammonio-cupric sulphate, and tetrabasic cupric sulphate:





*Sulphate of Cupricum and Cuprammonium*,  $\text{NH}^3\text{Cu}^2\text{SO}^4$ , or  $\left. \begin{matrix} (\text{NH}^3\text{Cu}) \\ \text{Cu} \end{matrix} \right\} \text{SO}^4$ , is the residue obtained by gently heating anhydrous cupric sulphate saturated with ammonia, or by gradually heating tetrammonio-cupric sulphate to  $149^\circ \text{C}$ . (Gm. v. 450.)

*Diammonio-cupric Nitrate*, or *Nitrate of Ammo-cuprammonium*,  $2\text{NH}^3\text{CuNO}^3$ , is obtained by saturating a hot concentrated solution of cupric nitrate with ammonia-gas, and leaving the solution to crystallise by cooling. It forms blue needle-shaped crystals, which give off a little ammonia when heated, but no water if it has been previously well dried. At a higher temperature it explodes. It dissolves easily in water; a small quantity of acid added to the solution throws down a basic cupric nitrate. (Gm. v. 455.)

*Bromate of Ammo-cuprammonium*,  $2\text{NH}^3\text{CuBrO}^3$ , is precipitated in dark blue needles and as a crystalline powder, on adding alcohol to an ammoniacal solution of cupric bromate. It turns green when exposed to the air, dissolves in a small quantity of water, but is decomposed by a larger quantity, with precipitation of cupric hydrate. (Gm. v. 463.)

The corresponding *iodate* is formed in a similar manner.

*Tetrammonio-cupric Hyposulphate*, or *Hyposulphate of Ammocuprammonium*,  $4\text{NH}^3\text{Cu}^2\text{S}^2\text{O}^6$ , is produced by supersaturating a somewhat dilute solution of cupric hyposulphate with ammonia. It crystallises in azure-blue rectangular tables, permanent in the air, sparingly soluble in water. (Gm. v. 448.)

The following salts have lately been obtained.

Silicate of cuprammonium . . . . .	$(\text{NH}^3\text{Cu})^2\text{Si}^2\text{O}^6$
Tungstate of cuprammonium . . . . .	$(\text{NH}^3\text{Cu})^2\text{W}^2\text{O}^6 + \text{H}^2\text{O}$
Metantimonate of cuprammonium . . . . .	$(\text{NH}^3\text{Cu})^2\text{Sb}^2\text{O}^7 + 4\text{H}^2\text{O}$
Pyrophosphate of cuprammonium . . . . .	$(\text{NH}^3\text{Cu})^2\text{P}^2\text{O}^7 + \text{H}^2\text{O}$
Orthophosphate of cupricum and cuprammonium . . . . .	$(\text{NH}^3\text{Cu})^2\text{Cu}^2\text{PO}^4$
Arsenate of cuprammonium . . . . .	$(\text{NH}^3\text{Cu})^2\text{H}^2\text{AsO}^4 + \text{H}^2\text{O}$
Acetate of cuprammonium . . . . .	$\text{C}^2\text{H}^3(\text{NH}^3\text{Cu})\text{O}^2 + \text{H}^2\text{O}$
Tartrate of cuprammonium . . . . .	$\text{C}^4\text{H}^4(\text{NH}^3\text{Cu})^2\text{O}^8$
Tartrate of ammocuprammonium . . . . .	$\text{C}^4\text{H}^4(\text{NH}^3\text{AmCu})^2\text{O}^8$
Succinate of ammocuprammonium . . . . .	$\text{C}^4\text{H}^4(\text{NH}^3\text{AmCu})\text{O}^6$
Anisate of ammocuprammonium . . . . .	$\text{C}^6\text{H}^7(\text{NH}^3\text{AmCu})\text{O}^8 + \text{H}^2\text{O}$

These salts are obtained either by saturating cupric salts with ammonia, or by decomposing monammonio-cupric sulphate,  $\text{NH}^3\text{Cu}^2\text{SO}^4$ , with barium salts.

Ethylamine seems to form cuprammoniums of analogous composition. (Hugo Schiff, Compt. rend. liii. 410; Ann. Ch. Pharm. cxiii. 36.)

**COPPER-FROTH.** A basic arsenate of copper,  $\text{Cu}^2\text{AsO}^4\cdot 2\text{CuHO} + \frac{7}{2}\text{aq.}$ , also called *Tyrolite* and *Pharmacosiderite*, found native at Falkenstein in the Tyrol, and other localities. (See TYROLITE.)

**COPPER-GLANCE.** Native cuprous sulphide (ii. 74).

**COPPER-GLANCE, ANTIMONIAL.** (See ii. 75.)

**COPPER, GREEN, or Chrysocola.** A native silicate of copper,  $\text{Cu}^2\text{SiO}^3 + \text{aq.}$ , occurring in Cornwall, Hungary, Siberia, South Australia, &c., and used as an ore of copper. (See SILICATES.)

**COPPER-MICA.** This term is applied to two very different substances, viz.:  
1. A native arsenate of copper of somewhat variable composition ( $\text{Cu}^2\text{AsO}^4\cdot 5\text{CuHO} + \text{aq.}$ ), also called *Tamarite* and *Chalcophyllite*. (See TAMARITE.)

2. A cuprous antimonite,  $3\text{Cu}^2\text{O}\cdot \text{Sb}^2\text{O}^3$ , or  $\text{Cu}^2\text{SbO}^3$ , which is sometimes found in refined copper prepared from antimonial ores, and renders it more cold-short than red-short. When copper of this description is dissolved in cold or slightly warmed nitric acid, the cuprous antimonite is left behind, in very thin, regular, six-sided laminae, translucent, having a gold-yellow colour, and becoming brown and opaque while hot. In the flame of the oxyhydrogen blow-pipe, they melt to a black-brown glass. With borax they exhibit a slight intumescence, and form a yellowish-brown glass, turning greenish-blue when mixed with nitre. Strong hydrochloric acid dissolves them more completely than any other acid. The compound gave by analysis (deducting small quantities of lead, silver, iron, silica, and alumina), 57.68 per cent.  $\text{Cu}^2\text{O}$ , and 42.32  $\text{Sb}^2\text{O}^3$  (calculation, 58.54  $\text{Cu}^2\text{O}$ , and 41.16  $\text{Sb}^2\text{O}^3$ ). (Hausmann and Stromeyer, Schw. J. xix. 241.)

*Copper-mica, nickeliforous* ( $7\text{Cu}^2\text{O}\cdot 5\text{Ni}^2\text{O}$ ). $\text{Sb}^2\text{O}^3$ ? This compound is obtained from copper smelted at Goslar. After the copper has been treated with dilute nitric acid, the copper mica is freed from arsenical oxide of antimony — proceeding from

antimonide of copper previously contained in the copper, and decomposed by the nitric acid—by digesting it in a mixture of hydrochloric and tartaric acid. In this manner 100 parts of highly micaceous copper yield 4.16 pts. of pure copper-mica. It forms pale greenish-yellow, translucent, strongly lustrous, regular six-sided laminae, which assume a transient yellow colour when heated. This compound neither fuses nor suffers any alteration at a red heat. With carbonate of soda on charcoal, it yields a white brittle metal, and covers the charcoal with antimonic oxide. Heated in the outer blowpipe-flame with borax or microcosmic salt, it dissolves immediately, and forms a light green glass. It is scarcely attacked by acids, excepting by concentrated hydrochloric acid, which dissolves it after long boiling. When hydrogen gas is passed over 100 pts. of red-hot copper-mica, a quantity of water is obtained corresponding to 18.19 per cent. of oxygen. (In this reaction 2.55 pts. of the mica—that which contains only nickel and no copper—appear to escape decomposition.) The residue is baked together, but still retains the form of laminae; it may be decomposed by nitric acid or by chlorine; in either case, the pure nickel-mica remains undecomposed.

Nickeliferous copper-mica gives by analysis (abstracting the nickel-mica) 44.28 per cent.  $\text{Cu}^2\text{O}$ , 30.61  $\text{Ni}^2\text{O}$ , and 25.11  $\text{Sb}^2\text{O}_3$ , the above formula requiring 45.13  $\text{Cu}^2\text{O}$ , 30.21  $\text{Ni}^2\text{O}$ , and 24.66  $\text{Sb}^2\text{O}_3$ . (Boucher, Pogg. Ann. xli. 335.)

**COPPER-NICKEL.** Native arsenide of nickel. (See NICKEL.)

**COPPER-PYRITES.** (See SULPHIDES OF COPPER AND IRON, ii. 77.)

**COPPERAS.** Protosulphate of iron. (See SULPHATES.)

**COPROLITES.** The excrements of extinct animals, found in large quantities in certain geological formations, especially in the lias. Their true nature was first pointed out by Buckland. They consist mainly of phosphate and carbonate of calcium, the quantity of phosphate sometimes amounting to between 80 and 90 per cent.; they contain also magnesia, oxide of iron, silica, water, and organic matter, with small quantities of manganese and fluorine. Their composition is, in fact, very much like that of bone, the bony constituents of the excrements having resisted the action of decomposing agents more than the other portions. The quantity of phosphoric acid in coprolites renders them very valuable as manure.

*Analyses of Coprolites.*

	T. J. HERAPATH (a).				T. S. HUNT (b).			DANA (c).	REES (d).	WOLFF (e).	HANSEN (f).	MEUVI (g).
	From the coast of Suffolk.				From the Lower Silurian strata of Canada.			From Sandstone in the Connecticut Valley.	From Bituminous Shale in Bohemia.	From Rothensburg on the Taubor.	From Lignite near Roth, in the Rhongeburg.	From the Chalk near Rethel, in France.
Phosphoric anhydride	70.9	15.85	60.8	67.53	40.34	36.38	44.70	39.60	24.43	55.8	45.58	21.29
Phosphate of calcium $\text{Ca}^2\text{PO}_4$												
Phosphate of magnesium $\text{Mg}^2\text{PO}_4$	trace											
Phosphate of aluminium	1.6	4.71									2.04	
Ferric phosphate	6.9	9.2	4.1								27.71	
Fluoride of calcium	0.61	1.7										
Carbonic anhydride.									13.29		7.68	17.50
Carbonate of calcium	10.28	39.5	23.7	4.35	5.14	5.00	6.60	34.77		4.5		
Carbonate of magnesium	trace	0.5		1.65	9.70	7.02	4.76					
Protoxide of iron				2.95	12.62		8.60					
Lime									49.70		4.20	50.50
Magnesia									5.03		1.34	3.20
Sesquioxide of iron			2.0							8.0	0.62	
Alumina		6.2										
Sesquioxide of manganese	trace											4.80
Silica	5.79	10.6	1.6							9.7		
Sand				21.10	25.44	49.90	27.90	13.10		13.7		
Sulphate of calcium	trace		1.8					1.75				
Sulphate of potassium										5.8		
Chloride of sodium								0.50	7.55			
Soluble salts	traces	traces	traces									
Water	4.00			2.15	2.13	1.7	5.00	7.30			7.50	1.00
Organic matter		11.60	6.1									
Urate of ammonium and lime								3.00			3.33	
	100.08	99.87	100.1	99.73	100.00	97.56	100.02	100.00	97.5	100.00	98.29	

a Ann. Ch. Pharm. lxxix. 1.

c Pogg. Ann. cv. 155.

e Sil. Am. J. [2] xv. 126.

g Wien. Akad. Ber. xviii. 124.

b Ibid. lxxix. 221.

d Chem. Gaz. 1849, 449.

f Jahrb. Miner. 1847, 729.



The chalk marl and adjoining strata are also very rich in coprolites and other petrifications containing phosphoric acid, as shown by the following analyses made by Messrs. J. M. Paine and J. T. Way (Journ. Roy. Agr. Soc. vol. ix. pt. 1):

a. The chalk marl with fossils containing a large quantity of phosphoric acid. b. The marl itself from which the petrifications have been separated by sifting. c. Indurated marl and small fossils which remained on the sieve. d. Marl from Bentley with the fossils. e. The fossils therefrom. f. Petrifications in the upper marly layer of the Upper Greensand. g. Soft amorphous bodies in the same. h. Petrifications in the Gault, very rich in phosphoric acid. i. Petrifications at the junction of the Gault with the Lower Greensand. k. A conglomerate of petrifications with sandstone cement. l. Green granules from the Lower Greensand.

*Petrifications in the Chalk Marl and adjoining Strata.*

	a.	b.	c.	d.	e.	f.	g.	h.	i.	k.	l.
Phosphoric acid, (P <sub>2</sub> O <sub>5</sub> )	1.82	6.61	9.31	33.03	24.28	29.87	27.13	0.64	20.80	6.89	20.65
Carbonic acid (CO <sub>2</sub> )	28.98	2.61	2.35	8.38	12.43	8.77	8.77	8.64	1.06	4.52	4.01
Sulphuric acid (SO <sub>3</sub> )											5.13
Soluble silica	0.45	29.14	26.30	3.27			3.28	8.12	3.25	18.42	18.58
Insoluble silica	19.64	32.81	26.83	7.12	0.91	7.68	7.18	75.46	43.87	39.59	34.61
Lime	37.71	9.53	15.24	46.50	47.46	42.29	39.85	2.01	23.86	9.11	24.61
Magnesia	0.68	1.97	1.43	trace	0.21		0.96	0.18	0.57	1.64	
Alumina											0.98
Sesquioxide of iron	3.04	11.46	13.11	1.96	2.91	6.87	10.60	5.59	3.35	13.55	7.24
Potash		3.10									1.79
Soda											1.87
Water, organic matter, fluo- rine, and loss		3.02	2.64	3.04	11.80	4.52	2.49	2.30	3.40	4.12	2.28
	98.32	100.25	97.21	100.50	100.00	100.00	100.26	99.94	99.96	97.84	97.14

**COPULA.** See CONJUGATED COMPOUNDS (ii. 8).

**COQUIMBITE.** *White Copperas.*—A hydrated ferric sulphate found in the district of Copiapo in the province of Coquimbo, Chile, apparently produced by the weathering of iron pyrites. It forms crystals belonging to the hexagonal system, namely, small six-sided prisms with truncated pyramidal summits,  $\infty P.P.O.P.$  Angle of the terminal edges =  $128^{\circ} 8'$ ; of the lateral edges =  $68^{\circ}$ . Cleavage imperfect, parallel to the prismatic faces. Also in fine-grained masses. Specific gravity = 2—2.1. Hardness = 2.25. Colour white, inclining to brown, yellow, green, and sometimes blue. Lustre vitreous. Transparent or translucent. Taste astringent. Before the blowpipe it first gives off water, then sulphurous acid, and leaves a residue of ferric oxide. It dissolves in cold water and in hydrochloric acid, leaving only a small quantity of silica. The aqueous solution deposits a large quantity of ferric oxide on boiling.

Analyses by H. Rose (Pogg. Ann. xxvii. 310):

	SO <sub>3</sub>	Fe <sup>2</sup> O <sub>3</sub>	Al <sup>2</sup> O <sub>3</sub>	Ca <sup>2</sup> O	Mg <sup>2</sup> O	SiO <sub>2</sub>	H <sub>2</sub> O
Crystalline	43.65	24.11	0.92	0.73	0.32	0.31	30.10 = 100.04
Granular	43.65	25.21	0.78	0.14	0.21	0.37	29.98 = 100.24

These analyses agree nearly with the formula:



[if  $\text{Fe} = \frac{3}{2}\text{Fe} = 18\frac{1}{2}$ ], which requires 42.7 SO<sub>3</sub>, 28.5 Fe<sup>2</sup>O<sub>3</sub>, and 28.8 water.

The same salt has been found, also in hexagonal crystals, by Scacchi in the Phlegrean Fields, together with Halotrychin. Rammelsberg (*Mineralchemie*, p. 274) also regards as coquimbite, a mineral from Coquimbo, formerly called *Blakeite*, analysed by Blake (Journ. Bost. Soc. Nat. Hist.), and found to contain 41.37 per cent. SO<sub>3</sub>, 26.79 Fe<sup>2</sup>O<sub>3</sub>, 1.05 Al<sup>2</sup>O<sub>3</sub>, 0.30 Mg<sup>2</sup>O, 0.82 SiO<sub>2</sub>, and 29.40 water, which agrees nearly with the preceding formula; but it crystallises in regular octahedrons. Dana suggests that it may be an iron alum.

**CORACITE.** A mineral found on the north coast of Lake Superior, where it forms beds 2 inches thick in syenite. It is amorphous, with rough, conchoidal, resinous fracture. Colour black with grey streak. Specific gravity 4.378. Hardness 4.5. Heated alone before the blowpipe it remains unaltered; with fluxes it gives the reactions of uranium. It appears to be a variety of pitchblende, in which the uranic oxide is partly replaced by alumina (Leconte, Sill. Am. J. [3] iii. 173;

Jahresber. d. Chem. i. 1847-48, 1167). An analysis by Whitney (Sill. Am. J. [2] vii. 434) gave:

U <sup>4</sup> O <sup>3</sup>	Al <sup>4</sup> O <sup>3</sup>	Fe <sup>4</sup> O <sup>3</sup>	Pb <sup>2</sup> O	Ca <sup>2</sup> O	CO <sup>2</sup>	SiO <sup>2</sup>	HO	Total.
59.30	0.90	2.24	5.36	14.44	7.47	4.35	4.64	= 98.70

**CORAL.** Coral rocks consist mainly of carbonate of calcium, with variable quantities of carbonate of magnesium and organic matter, and small quantities of phosphate, sulphate, and fluoride of calcium, alkaline chlorides, oxide of iron and silica. Silliman found in fresh corals only 1 per cent. of magnesia, but in dense coral rock the carbonate of magnesium was found to amount to 38.07 per cent. Another rock, consisting of the debris of corals contained 5.29 per cent. carbonate of magnesium. The presence of the magnesia appears to be due to a double decomposition taking place between the original carbonate of calcium of the rock, and the magnesian salts in sea-water, a process which likewise contributes to the hardening of the rock. (Jahresber. d. Chem. 1847-8, 1291.)

B. Silliman, jun. (Sill. Am. J. [2] xii. 174), found in a considerable number of reef-forming corals, from 2.11 to 9.43 per cent. organic matter; the residue left after the removal of this contained from 97 to 99 per cent. carbonate of calcium, together with soluble silica, lime probably in combination with silica, also carbonate of magnesium, and the other salts above-mentioned.

The red pigment of corals is, according to Trommsdorff, not ferric oxide, but a red resin soluble in oil of turpentine, and after removal from the coral by this solvent, easily soluble also in alcohol and ether, but insoluble in caustic potash. In a red madrepora, Vauquelin found a red colouring matter, which was turned violet by alkalis.

The organic matter of the stems of polypes appears in some cases to consist of chitin or conchiolin.

In *Corallium nobile*, Forchhammer found 2.13 per cent., in *Isis hippurites*, 6.32 per cent. carbonate of magnesium. In *Corallium rubrum* and *Madrepore oculata*, Stratingh and Fyfe found a trace of iodine.

Respecting the composition and alterations of coral rocks, see also Dana (Sill. Am. J. [2] vi. 268). Forchhammer (J. pr. Chem. xlix. 52; Chem. Gaz. 1849, 411).—Damour (Ann. Ch. Phys. [3] xxxii. 362). Dana (*ibid.*, 410).—Also Jahresber. d. Chem. 1847-8, p. 1291; 1849, p. 813; 1851, p. 865; 1852, pp. 958-961.

**CORALLINA OFFICINALIS.** *Nodularia officinalis*, *Muscus corallinus s. marinus*.—The shell of a marine radiate animal, formerly used in medicine. According to an analysis by Bouvier (Ann. Chim. viii. 308), it consists of 61.6 per cent. carbonate of calcium, 7.4 carbonate of magnesium, 0.3 gypsum, 1.9 chloride of sodium, 0.2 ferric oxide, 6.6 gelatinous matter, 6.4 albumin, and probably also iodine and bromine. It was used comminuted and mixed with other corals, viz. *C. fragilissima*, *C. cylindrica*, *C. moniformis*, &c.

**CORDERITE.** Syn. with DICHOITE.

**CORIANDER, OIL OF.** (Trommsdorff, Arch. Pharm. [2] ii. 114.—Kawalier, J. pr. Chem. lxxviii. 226.)—Coriander seeds, the fruit of *Coriandrum sativum*, contain about 0.37 per cent. of a volatile oil, besides fat, extractive matter, &c. The volatile oil, which is obtained by distilling the bruised fruit with water, is colourless or pale yellow, has an aromatic taste, and when concentrated, smells like the seeds, though more agreeably; in the dilute state it smells like orange-flowers. Specific gravity 0.859 (Trommsdorff), 0.871 at 14° C. (Kawalier). It dissolves in alcohol, ether, and oils, both fixed and volatile. It explodes violently with iodine. With strong nitric acid, it becomes very hot, and forms a resinous mass. Strong sulphuric acid converts it into a brown-red liquid, which carbonises quickly when heated.

Coriander oil is a mixture of several oils, and appears to vary in composition. It contains a volatile oxygenated oil, and a less volatile oil containing little or no oxygen. The crude oil begins to boil at 150° C., an oil then passing over corresponding in composition to the formula C<sup>10</sup>H<sup>18</sup>O, or C<sup>20</sup>H<sup>36</sup>O<sup>2</sup>; afterwards the temperature rises, and a less volatile oil distils over, containing, according to Kawalier, C<sup>10</sup>H<sup>22</sup>O, or perhaps 2C<sup>20</sup>H<sup>36</sup>.HO, or 4C<sup>10</sup>H<sup>16</sup>.H<sup>2</sup>O. The crude oil distilled with phosphoric anhydride yields a distillate of camphene, C<sup>10</sup>H<sup>18</sup>.

Coriander-oil saturated at a low temperature with hydrochloric acid gas, forms a permanent liquid hydrochlorate, which may be purified by washing with weak soda-ley, and drying over chloride of calcium. According to Kawalier, it contains C<sup>10</sup>H<sup>22</sup>.O.Cl<sup>2</sup>, or perhaps 4(C<sup>10</sup>H<sup>16</sup>.HCl) + H<sup>2</sup>O.

**CORIARIN.** A crystalline substance said to exist in the leaves of *Coriaria myrtifolia*. (Peschier, Trommsd. N. J. xvi. 57.)



**CORK.** The outer bark of the *Quercus suber*, a tree which grows to the height of 30 or 40 feet, in the South of Europe, in the North of Africa, and in the East. It is distinguished by peculiar toughness, softness, and elasticity, which render it indispensable for a variety of purposes.

Cork consists for the most part of a modified form of cellulose, called *suberin*, which remains behind after the cork has been exhausted with alcohol, ether, water, and sulphuric acid.

Chevreul also found in cork a fragrant substance, *cerin* (i. 830), which passed over on distilling the cork with water, a soft resin, a yellow and a red colouring matter, quercitanic acid, gallic acid, and a brown nitrogenous substance, together with 0.7 per cent. calcium, salts of vegetable acids, and 4 per cent. water, which is given off at 100° C.

Cork oxidised with nitric acid yields oxalic, suberic, and ceric acids (i. 830).

**CORK, MOUNTAIN.** See **ASBESTOS** (i. 416).

**CORNFELD.** A compact hornblende rock, of smooth fracture, extremely tough, and sonorous when struck.

**CORNEOUS LEAD.** Native chloro-carbonate of lead,  $2\text{PbCl.Pb}^2\text{CO}^3$ ; also called *cerusina*. (See **LEAD**, **CHLORIDE OF**.)

**CORNIN**, or **CORNIC ACID.** A crystallised bitter substance, obtained from the root of *Cornus florida*, by exhausting the root with water, mixing the solution with moist hydrate of lead, evaporating the filtrate to an extract, treating the residue with absolute alcohol, mixing the turbid solution with ether, digesting the filtrate with carbonate of lead, filtering again, distilling off the greater portion of the liquid, and leaving the remaining turbid liquid to evaporate. Cornin is then deposited after 12 hours, in stellate groups of delicate crystals having a satiny lustre.

Cornin dissolves easily in water and in alcohol, sparingly in ether. The solutions are not precipitated by alkalis, tincture of galls, iron-salts, barium-salts, or neutral lead-salts, but give precipitates with basic acetate of lead, and nitrate of silver. Cornin does not exhibit basic properties; it is partly separated from its solutions by charcoal, either vegetable or animal, so that these substances cannot be used to decolorise the solutions. (Geiger, Ann. Ch. Pharm. xiv. 206.)

**CORNETE.** A name sometimes applied to the compact felspar which constitutes the base of porphyry.

**CORNOVIN.** A resin obtained from the bark of an East Indian tree, called *Coroa* or *Cornova*. It is brownish-yellow, of oily consistence, inodorous, has a rough irritating taste, and acid reaction. It dissolves easily in absolute alcohol and in ether, but not in oils. (Trommsdorff, Trommsd. N. J. xxi. 2, 116).

**CORNUBIANITE.** A fine-grained modification of gneiss, occurring in Cornwall and in the Erzgebirg. It is of a dingy, greenish, yellowish, or reddish-grey colour, striated and spotted. The stratification is indistinct, and recognisable only by the layers of mica, or by the variations of colour and fineness of grain. (Kopp, Handw. d. Chem. ii. [3] 212.)

**CORNUS.** The following species of this genus of plants have been chemically examined. They do not appear to contain any alkaloids.

*Cornus florida*.—The bark of this tree, which is used in North America as a febrifuge, contains a bitter crystalline substance, *cornin*,—a tannin which turns iron-salts blue,—an indifferent crystalline resinous body,—gum,—a small quantity of starch,—a colouring matter containing iron and manganese, and lime and magnesia in combination with oxalic acid, and perhaps also with malic and phosphoric acids. The fruit is scarlet-coloured and very bitter.

*Cornus mascula*.—The unripe fruits contain a large quantity of tannin; the riper fruits are sweet.

*Cornus sanguinea* (*Dog-wood*).—The fruits, which are very bitter, yield oil when pressed. (Rochleder's *Phytochemie*, p. 116).

**CORNWALLITE.** An arsenate of copper from Cornwall, containing, according to Lerch, 30.21 per cent.  $\text{As}^2\text{O}^3$ , 2.16  $\text{P}^2\text{O}^5$ , 54.61  $\text{Cu}^2\text{O}$ , and 13.02 water, therefore  $56\text{Cu}^2\text{O}.4\text{As}^2\text{O}^3 + 5\text{H}^2\text{O}$ , or  $\text{Cu}^2\text{AsO}^4.\text{Cu}^2\text{O} + \frac{5}{2}\text{H}^2\text{O}$ . Amorphous. Dark green. Specific gravity = 4.166. Hardness = 4.5 (Handw. d. Chem. ii. [3] 212).

**CORTEPINITANNIC ACID.** An acid obtained, together with several other substances, from the bark of the Scotch fir (*Pinus sylvestris*). Dried in vacuo, it forms a red powder containing  $\text{C}^{18}\text{H}^9\text{O}^7 + 3\text{HO}$ . Its aqueous solution forms

a deep green colour with sesquichloride of iron. (Kawalier, Ann. Ch. Pharm. lxxxviii. 360.)

**CORTICIN.** An amorphous yellowish substance existing in the bark of the aspen (*Populus tremula*), and perhaps also in other barks. It is tasteless and inodorous, sparingly soluble in water, easily in alcohol and in acetic acid, and is precipitated from the latter solution by water or sulphuric acid. (Braconnot, Ann. Ch. Phys. [2] xliv. 296.)

**CORUNDELLITE.** See MARGARITE.

**CORUNDOPHILITE.** A hydrated silicate of aluminium and iron, found with corundum in stellate groups at Ashville, Buncombe County, North Carolina. The crystalline form is said to be monoclinic. An analysis (made with only 0.146 gm. of material) gave 34.75 per cent.  $\text{SiO}_2$ , 31.25  $\text{Fe}_2\text{O}_3$ , 8.55  $\text{Al}_2\text{O}_3$ , 5.47 water, and about 2.0 per cent. alkali. (C. U. Shepard, Sill. Am. J. [2] xii. 201.)

**CORUNDUM.** *Sapphire, Ruby, Oriental Amethyst, Oriental Topaz, Adamantine spar, Emery, (Korund, Smirgel, Demantspath, Salamstein, Telksic, Corindon, Rubis d'Orient).*—Native anhydrous alumina,  $\text{Al}_2\text{O}_3$ . Crystallises in the hexagonal system, isomorphous with the sesquioxides of iron and chromium. Primary form an acute rhombohedron R. Numerous combinations occur, among which may be mentioned R. oR, (figs. 146, 147) and  $\infty\text{P}2 \cdot \text{oR} \cdot \text{R} \cdot \frac{1}{3}\text{P}2$  (fig. 148).

Fig. 146.



Fig. 147.

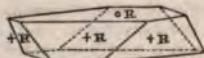
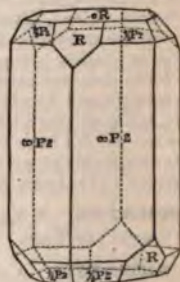


Fig. 148.



For the primary form R, the ratio of the vertical to the horizontal axis is as 1.3617 : 1. Angle of the terminal edges =  $86^\circ 6'$ . For  $\frac{1}{3}\text{P}2$  the angle of the terminal edges =  $128^\circ 3'$ , and of the lateral edges =  $122^\circ 18'$ . Cleavage imperfect, parallel to R and oR; where it appears perfect, it is probable that combination-faces of different individuals are present. Twin crystals also occur united by the faces R or oR (*Kopp's Krystallographie*, p. 211). Corundum occurs also massive, granular, or impalpable, often in layers, from composition parallel to R.

Specific gravity = 3.9 to 4. Hardness = 9.0. Colour, nearly white, grey, blue (sapphire), red (ruby), violet, yellow, and brown. Lustre vitreous, sometimes pearly on the basal planes oR. Transparent in various degrees down to mere translucence on the edges. Some crystals exhibit a bright opalescent six-sided star when viewed in the direction of the vertical axis (*asteria*). Fracture conchoidal, uneven, or splintery. Brittle.

Corundum is infusible and unalterable before the blowpipe. The powder moistened with cobalt-solution and ignited exhibits a fine blue colour. With borax it slowly forms a clear glass; does not melt with soda. Insoluble in acids, but, by fusion with acid sulphate of potassium, it yields a mass easily soluble in water.

Pure corundum consists entirely of alumina, but it is often mixed with ferric oxide, titanous acid, and other substances, which affect its colour and transparency. *Precious corundum* includes the transparent varieties of pure and brilliant colour, which are cut for gems; the blue variety is sapphire, the red, ruby, the yellow Oriental topaz, the violet Oriental amethyst. *Common corundum* includes the opaque varieties of less pure colour, viz. adamantine spar, which is crystallised and yields a very hard powder, used for polishing diamonds and other gems, and emery, which has a crystallo-granular structure, and is used in like manner for polishing metals, glass, &c.

The following are analyses of corundum by J. L. Smith (Sill. Am. J. [2] x. 354; xi. 53; Dana, ii. 112). Mag. stands for magnetic oxide of iron.



	Hard- ness.	Spec. grav.	Al <sub>2</sub> O <sub>3</sub> .	Mag.	CaO.	SiO <sub>2</sub> .	Water.
Sapphire (Indian)	100	4.06	97.51	1.89	. .	0.80	. . = 100.20
Ruby (Indian)	90	. .	97.32	1.09	. .	1.21	. . = 99.62
Corundum of Asia Minor	77	3.88	92.39	1.67	1.12	2.05	1.60 = 99.83
" Nicaria	65	3.92	87.52	7.50	0.82	2.01	0.68 = 99.53
" Asia	60	3.60	86.62	8.21	0.70	3.85	1.16 = 101.94
" India	58	3.89	93.12	0.91	1.02	0.96	2.86 = 98.87
" "	55	3.91	84.56	7.06	1.20	4.00	3.10 = 99.92
Emery	. .	. .	. .	Fe <sub>2</sub> O <sub>3</sub>			
Kulah	57	4.28	63.50	33.25	0.82	1.61	1.90 = 101.18
Samos	56	3.98	70.10	22.21	0.62	4.00	2.10 = 99.03
Nicaria	56	3.75	71.06	20.32	1.40	4.12	2.53 = 99.43
Kulah	53	4.02	63.00	30.12	0.50	2.36	3.36 = 98.34
Gumuch	47	3.82	77.82	8.62	1.80	8.13	3.11 = 99.48
Naxos	46	3.75	68.53	24.10	0.86	3.10	4.72 = 101.31
Nicaria	46	3.74	75.12	13.06	0.72	6.88	3.10 = 98.83
Gumuch	42	4.31	60.10	33.20	0.48	1.80	5.62 = 101.20
Kulah	40	3.89	61.05	27.15	1.30	9.63	2.00 = 101.13

Corundum occurs associated with crystalline rocks. The sapphire, ruby, and other forms of precious corundum, are obtained chiefly from India, China, and Ceylon. Sapphire has been found also at Newton, New Jersey, and a fine ruby in Cherokee County, Georgia (U. S.). Adamantine spar is obtained from China and from the Ural; emery from the island of Naxos, from Smyrna, from Schwarzenberg in Saxony, from the Ural, Spain, Greece, and other places. A boulder of blue massive corundum has been found in Buncombe County, North Carolina. Corundums are also found in numerous other localities imbedded in granite, gneiss, syenite, mica-slate, dolomite, basalt, and other rocks, but seldom large or fine enough to be fit for gems.

Corundum sometimes absorbs water and changes to diaspor. It is also replaced by silica, forming quartz pseudomorphs.

**CORYDALINE.** An alkaloid existing in the roots of *Corydalis bulbosa*, *C. fabacea*, and *Aristolochia cava*. It was discovered by Wackenroder (Kastn. Arch. [1826] Bd. viii.), and afterwards examined by Peschier (Trommsd. N. J. xvii. 80), Winckler (Pharm. Centr. 1832, p. 38), Ruickholdt (Ann. Ch. Pharm. lxiv. 369), and Müller (Vierteljahrsschrift pr. Pharm. viii. 526).

**Preparation.**—1. From *Corydalis bulbosa*. The juice expressed from the fresh root is coagulated by heat, precipitated with neutral acetate of lead, and filtered; the lead is separated by sulphuric acid; and the corydaline is precipitated from the filtrate by ammonia, then dried and dissolved in 12 to 16 pts. of alcohol of 80 per cent.; and the solution, after being digested with blood-charcoal, is filtered and evaporated to the crystallising point. By mixing the alcoholic solution with a large quantity of water, the corydaline may be precipitated in the pulverulent form (Winckler). Müller exhausts the root with water containing hydrochloric acid; precipitates the filtrate with carbonate of sodium; redissolves the precipitate in hydrochloric acid; again precipitates with carbonate of sodium; exhausts the washed and dried precipitate with pure oil of turpentine; and agitates the oil with water containing hydrochloric acid. The corydaline then dissolves in the acid and may be precipitated by potash.

2. From the root of *Aristolochia cava*. The root is exhausted with water containing hydrochloric acid; the solution is precipitated by carbonate of sodium; the precipitate treated with alcohol; and the solution left to crystallise by evaporation. This is the easiest mode of preparation. (Ruickholdt.)

**Properties.**—Corydaline forms light, non-coherent, greyish-white masses, which stain strongly. According to Müller, it is a loose white powder. It is usually said to be tasteless and inodorous, but according to Müller it is bitter when moist. It is insoluble in water, but easily soluble in strong alcohol and ether. From a hot saturated alcoholic solution, it crystallises in shining rhombic prisms; by spontaneous evaporation in scales. Corydaline melts at 100° C. (at 60°—70°, according to Müller); when strongly heated, it turns brown and gives off water and ammonia. Nitric acid colours it deep red, the colour being perceptible even in very dilute solutions. Sulphuric acid dissolves it with deep yellowish-red colour.

Corydaline gives by analysis:

C	H	N	O	
62.4	6.8	4.3	26.5	= 100 (Döbereiner).
60.2	5.9	3.0	30.9	= 100 (Ruickholdt).

Hence have been deduced the empirical formulæ  $C^{14}H^{12}NO^{10}$  (Döbereiner);

$C^{10}H^{12}NO^3$  (Ruickholdt); Müller, from his own analysis, calculates the formula  $C^{10}H^{12}NO^3$ . None of these formulæ can be depended upon, as there is no proof that the analyses were made with pure substances.

Corydaline unites with acids, forming salts most of which are colourless and some crystalline (according to Müller, none of them crystalline). They have a very bitter taste and are precipitated by *tannic acid* and by *ammonia*; also by *potash* or *soda*; but the precipitate redissolves in excess of the fixed alkali.

*Hydrochlorate of Corydaline* forms yellowish-green, brittle, right rhombic prisms with perpendicular terminal faces having a glassy lustre. It contains 10·8 per cent. HCl, and 16·5 per cent. crystallisation-water, and is therefore perhaps  $C^{10}H^{12}NO^3 \cdot 2HCl + 12HO$  (Ruickholdt). The crystals give off 12·5 per cent. water at  $100^\circ C$ , and 3·0 per cent. more at  $145^\circ$ ; at higher temperatures decomposition takes place. The salt dissolves readily in water and in strong alcohol.

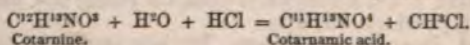
*Hydrochlorate of corydaline* forms a white bulky precipitate with *mercuric chloride*.

*Acetate of Corydaline* is easily soluble and crystallisable; so likewise is the *neutral sulphate*; with excess of sulphuric acid, a gummy acid salt is obtained by evaporation.

**CORYDALIS BULBOSA.** In the root of this plant, corydaline was first found by Winckler; afterwards fumaric acid by Wicke (Ann. Ch. Pharm. lxxxvii. 225). Müller (Vierteljahr. pr. Pharm. viii. 526), who has examined the root more minutely, finds no fumaric acid. By distilling the root with water, he obtained a volatile oil and acetic acid; ether extracted from the dried root 2·2 pts. consisting of colouring matter, fixed oil, resin, and a small quantity of corydaline; alcohol extracted 24·6 pts. (corydaline, resin, citric, malic, acetic, tannic and saccharic acids); water extracted 3·4 pts. (albumin, starch, and a small quantity of valeric acid); and hydrochloric acid, 15·5 pts. (pectin and oxalate of calcium), the residue, amounting to 54·2 pts., consisted of a woody fibre and other insoluble matters. The dried root yielded 5·9 per cent. ash, containing in 100 pts. 5·2 pts.  $K^2O$ , 10·4  $Na^2O$ , 8·3  $Ca^2O$ , 7·5  $Mg^2O$ , 3·8  $Al^2O^3$ , 4·1  $Fe^2O^3$ , 0·1  $Mn^2O^3$ , 11·3  $SiO^2$ , 9·3  $P^2O^5$ , 2·0  $CO^2$ , and 2·3 Cl.

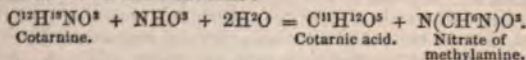
**COSSEINE.** A name applied by Martin to an organic base, which he supposes to exist in kousso, the celebrated Abyssinian remedy for tape-worm. Martius, however (Buchner's N. Repert. [2]. iii. 177), was not able to find it.

**COTARNAMIC ACID,**  $C^{11}H^{13}NO^4$ , is formed by the action of aqueous hydrochloric, hydriodic, or sulphuric acid on cotarnine, at a temperature of  $140^\circ$  or  $150^\circ C$ .



Like aspartic acid, cotarnamic acid combines with strong mineral acids. The only compound of it which has as yet been obtained pure is the *hydrochlorate*,  $C^{11}H^{13}NO^4 \cdot HCl$ . This body crystallises in small, pale yellow tufts of silky needles; it is but slightly soluble in cold water, very soluble in hot water; it is less soluble in alcohol and insoluble in ether. When the pure compound is dissolved in hot water, a portion always decomposes, causing an orange precipitate (of cotarnamic acid) to separate; the same precipitate is produced on cautiously adding ammonia or potash to the solution; the hydrochlorate dissolves without alteration in water containing a little free hydrochloric acid. An aqueous solution exposed to the air gradually acquires a beautiful green colour. Nitric acid, added drop by drop to a solution of this compound in hot water, causes it to appear deep opaque crimson by reflected light, and orange-yellow by transmitted light. Evaporated on a water-bath with sulphuric acid, it acquires a fine crimson colour when nearly dry; this colour is destroyed by addition of water, but reappears when the water is again evaporated. (Matthiessen and Foster, *private communication*.) G. C. F.

**COTARNIC ACID,**  $C^{11}H^{13}O^3$ .—This substance is produced by the action of dilute nitric acid on cotarnine at a gentle heat (Matthiessen and Foster, Proc. Roy. Soc. xi. 59), but the conditions necessary for its certain production are not yet known. Methylamine is formed at the same time:



It dissolves easily in water, giving a solution which reacts strongly acid with litmus. Alcohol dissolves it but sparingly, and ether precipitates it from its alcoholic solution. It gives white precipitates with *acetate of lead* and *nitrate of silver*. The *silver-salt* is slightly more soluble in hot water than in cold; it contains  $C^{11}H^{13}Ag^2O^3$ .

Cotarnine may be regarded as the methylated *imide* corresponding to cotarnic acid. Cotarnic acid, cotarnamic acid, and cotarnine then bear to each other the same relations as malic acid, aspartic acid, and malanile or phenylmalimide:



Cotarnic acid .	$C^{11}H^{12}O^3$	Malic acid .	$C^4H^5O^3$
Cotarnamic acid .	$C^{11}H^{12}NO^4$	Aspartic acid .	$C^4H^7NO^4$
Cotarnine .	$C^{11}H^{10}(CH^3)NO^3$	Malanile .	$C^4H^4(C^2H^3)NO^3$

G. C. F.

**COTARNINE**,  $C^{11}H^{10}NO^3 + H^2O$ , or  $C^4H^3NO^3 + 2HO$ .—A non-volatile organic base, obtained by the action of oxidising agents on narcotine. It was first obtained by Wöhler, in 1844 (Ann. Ch. Pharm. l. 19), as a product of the oxidation of narcotine by peroxide of manganese and sulphuric acid; and, almost simultaneously, Blyth (*ibid.* l. 37; Mem. and Proc. Chem. Soc. ii. 168) observed its formation by the action of dichloride of platinum on narcotine. Cotarnine has been further studied particularly by Anderson (Ed. Phil. Trans. xx. [3] 359; Chem. Soc. Qu. J. v. 266; Ann. Ch. Pharm. lxxxvi. 196), and by Matthiessen and Foster (Proc. Roy. Soc. xi. 55; Ann. Ch. Pharm. Supplement B. i. 330; Bullet. de la Société Chim. 1861, 22).

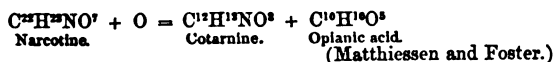
**Formation and preparation.**—1. Narcotine is dissolved in a considerable excess of dilute sulphuric acid (3 pts. sulphuric acid, 30 pts. water, and 2 pts. narcotine, are good proportions: Matthiessen and Foster, *private communication*), the solution heated to boiling, finely powdered peroxide of manganese (3 pts. Matth. and Foster.) added, and the liquid filtered as hot as possible. (Wöhler directs to boil the mixture with excess of peroxide of manganese and acid as long as gas is evolved; Matthiessen and Foster recommend to add the peroxide of manganese in the proportion given above, as quickly as possible, to the already boiling solution of narcotine, and to filter immediately.) The filtrate deposits opianic acid on cooling, and the mother-liquor poured off from the crystals contains sulphate of cotarnine and sulphate of manganese. The manganese is precipitated with carbonate of sodium, the precipitate filtered off, and the filtrate evaporated so as to cause the greater part of the sulphate of sodium contained in it to crystallise out; the addition of potash to the concentrated solution of sulphate of cotarnine then produces a brown granular precipitate of impure cotarnine, which is purified by solution in hydrochloric acid, treatment with animal charcoal, and reprecipitation by potash. Or, chloride of mercury or dichloride of platinum is added to the solution freed from manganese, whereby a precipitate of chloromercurate or chloroplatinate is obtained, which is washed, suspended in hot water, and decomposed with sulphydric acid; the filtrate is then mixed with excess of baryta-water and evaporated to dryness, and the cotarnine is dissolved out of the residue by alcohol. (Wöhler.)

2. Narcotine is boiled with an excess of dichloride of platinum and dilute hydrochloric acid. Red prismatic crystals of chloroplatinate of cotarnine are thus obtained. (Blyth.)

3. Anderson recommends, for the preparation of cotarnine, to act upon narcotine with dilute nitric acid (1 pt. narcotine, 3 pts. nitric acid of specific gravity 1·4, and 8 pts. water) at 49° C. The liquid separated from the teropiammonie (*q. v.*) which is thus formed, gives a crystalline precipitate of cotarnine on the addition of potash.

4. Narcotine treated as in the first method, acid chromate of potassium being however used in place of peroxide of manganese, yields cotarnine in a state of great purity. (Matthiessen and Foster.)

The formation of cotarnine from narcotine takes place according to the equation:



**Properties.**—Cotarnine forms small, colourless, needle-shaped crystals, grouped in stars. It is only slightly soluble in cold water, but somewhat more so in boiling water; alcohol dissolves it, forming a brownish solution, from which it cannot be obtained crystallised; it dissolves easily in ether and in ammonia; it is almost insoluble in caustic potash. It melts at 100° C., and loses 1 at. of water of crystallisation; at a higher temperature it is charred, and produces a disagreeable smell. Cotarnine has a bitter taste and faintly alkaline reaction.

Crystallised cotarnine contains:

	Calculated.	Blyth.	Matth. and Foster.
C <sup>12</sup> . .	144 . . 60·76 . .	61·41 . .	60·84 . . 60·55
H <sup>10</sup> . .	15 . . 6·33 . .	6·38 . .	6·53 . . 6·50
N . .	14 . . 5·91 . .	5·62 . .	5·82 . . 5·91
O <sup>4</sup> . .	64 . . 27·00 . .		
	237 . . 100·00		

Cotarnine dried at 100° contains:

	Calculated.		Blyth.	
C <sup>12</sup> . .	144 . .	65.75 . .	65.95 . .	
H <sup>12</sup> . .	13 . .	5.94 . .	6.39 . .	
N . .	14 . .	6.39 . .		
O <sup>3</sup> . .	48 . .	21.92 . .		
C <sup>12</sup> H <sup>12</sup> NO <sup>3</sup> . .	219 . .	100.00 . .		

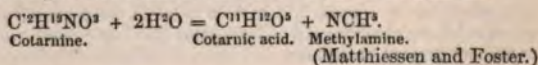
Water of crystallisation:

	Calculated.		Blyth.	
C <sup>12</sup> H <sup>12</sup> NO <sup>3</sup> . .	219 . .	92.41 . .		
H <sup>2</sup> O . . . .	18 . .	7.59 . .	7.51 . .	7.22
	237 . .	100.00 . .		

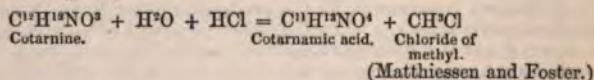
The formula originally proposed for cotarnine by Wöhler, was C<sup>20</sup>H<sup>12</sup>NO<sup>3</sup>; Blyth gave its formula as C<sup>23</sup>H<sup>12</sup>NO<sup>3</sup>; Gerhardt (*Précis de Chimie Organique*, 1845, ii. 298) adopted the expression C<sup>12</sup>H<sup>12</sup>NO<sup>3</sup> (= C<sup>20</sup>H<sup>12</sup>NO<sup>3</sup>); Wertheim (*Wien. Acad. Ber.* vi. 111), believing in the existence of several homologous varieties of cotarnine, gave the formula C<sup>12</sup>H<sup>12</sup>NO<sup>3</sup> (= C<sup>24</sup>H<sup>12</sup>NO<sup>3</sup>) for what he called *methyl-cotarnine*; Matthiessen and Foster regard cotarnine as always of the same composition, and represent it by the formula C<sup>12</sup>H<sup>12</sup>NO<sup>3</sup> = (C<sup>11</sup>H<sup>10</sup>O<sup>3</sup>)<sup>n</sup> CH<sup>1</sup> } N, that is, as *methyl-cotarnimide*. (See COTARNIC ACID.)

The aqueous solution of cotarnine precipitates ferrous and cupric salts; it gives no coloration with ferric salts (Blyth). It is also precipitated by tannin. (Wöhler.)

*Decompositions.*—1. *Nitric acid* dissolves cotarnine with red colour, and, if heated, oxidises it, forming oxalic acid, and afterwards apophylllic acid, (*g. v.*) (Wöhler, Anderson, Matthiessen and Foster.) Very dilute nitric acid, gently heated with cotarnine sometimes produces cotarnic acid, C<sup>11</sup>H<sup>12</sup>O<sup>3</sup>, and methylamine:



2. Heated with *hydrochloric*, *hydriodic*, or dilute *sulphuric acid* to 140° C. in a sealed tube, it yields chloride or iodide of methyl, or methyl-sulphuric acid, and cotarnamic acid, C<sup>11</sup>H<sup>12</sup>NO<sup>4</sup> (p. 88).



3. With *iodide of ethyl* at 100° C. it yields hydriodate of cotarnine, but no ethylised derivative. (How, *Ed. Phil. Trans.* vol. xxi.; *Ann. Ch. Pharm.* xcii.)

**SALTS OF COTARNINE.** The salts of cotarnine are for the most part very soluble; they are obtained directly, by solution of the base in dilute acids.

*Hydrochlorate of Cotarnine*, C<sup>12</sup>H<sup>12</sup>NO<sup>3</sup>.HCl (+ 2½H<sup>2</sup>O?), is obtained by evaporating its aqueous solution, in the form of long silky crystals, which are very soluble in water. It loses 14.88 per cent. of water at 100° (Blyth): the above formula corresponds to 14.97 per cent. Dried at 100° C. it contains, according to Blyth's analysis, 57.39 per cent. carbon and 5.73 hydrogen; the formula C<sup>12</sup>H<sup>12</sup>NO<sup>3</sup>.HCl requires 56.36 per cent. C, and 5.48 H.

*Chloroplatinate of Cotarnine*, C<sup>12</sup>H<sup>12</sup>NO<sup>3</sup>.HCl.PtCl<sup>2</sup>.—This salt forms, when precipitated in the cold, a lemon-yellow, crystalline precipitate, resembling chloroplatinate of ammonium; when hot solutions of hydrochlorate of cotarnine and dichloride of platinum are mixed together, the double salt separates as the mixture cools, in small, round, transparent nodules, of a reddish-yellow colour (Wöhler). It is obtained in the form of large, dark-red, six-sided prisms, by boiling a solution of narcotine in hydrochloric acid with an excess of dichloride of platinum (Blyth). This salt is very slightly soluble in cold water, but somewhat more so in hot water; it appears, however, to be altered by repeated solution in hot water. It can be boiled with ammonia without undergoing decomposition. Boiled with baryta-water, it is decomposed, and metallic platinum is precipitated.

It contains:



	Calculated.		Wöhler.		Blyth.		Matth. and Foster.		
C <sup>12</sup>	144	33.84	34.9	34.2	34.4	35.0			
H <sup>1</sup>	14	3.29	3.2	3.5	3.3	3.6			
N	14	3.29	4.4						
O <sup>8</sup>	48	11.28							
Pt	99	23.27	23.0	22.6	22.9	23.0	23.3	23.1	23.2
Cl <sup>2</sup>	106.5	25.03	24.1						
	425.5	100.00							

Blyth dried the salt for analysis at 100°; Matthiessen and Foster at the ordinary temperature, over sulphuric acid *in vacuo*; they could not obtain constant results with the salt dried at 100°.

It sometimes happens that the treatment of narcotine with dichloride of platinum gives rise to another chloroplatinate, which crystallises in long, bright, orange-yellow needles. This salt, which Blyth supposed to contain a peculiar alkaloid, which he named *narcogenine*,  $C^{12}H^{12}NO^8$ , is decomposed when boiled with ammonia, into narcotine and cotarnine, and is probably a double chloroplatinate of these two bases. Blyth's analytical results accord nearly with those required by the formula



*Chloraurate of Cotarnine* has a beautiful dark red colour.

*Chloromercurate of Cotarnine*,  $C^{12}H^{12}NO^8.HCl.2HgCl$ , forms a pale yellow precipitate, which gradually becomes crystalline. It is not precipitated from rather dilute warm solutions, but is deposited on cooling, in small pale yellow prisms. It appears to suffer decomposition by repeated crystallisation. It contains:

	Calculated.		Wöhler.	
Nitrogen . . . .	14	2.66	2.6	
Mercury . . . .	200	37.98	37.95	
Chlorine . . . .	106.5	20.23	20.68	G. C. F.

**COTTON.** The filamentous matter attached to the seeds of various species of *Gossypium*, a genus of plants belonging to the Malvaceous order. It consists of hairs springing from the surface of the seed-coat, and filling up the cavity of the seed-vessel in which the seeds lie. These hairs are long weak tubes, which, when immersed in water and examined under the microscope by transmitted light, look like flat, narrow, transparent ribands, entirely distinct from each other, and with a perfectly even surface and uniform breadth, rarely jointed, and if so, having the articulations perpendicular to the length of the tube. The individual tubes are very weak and fragile, and it is only when many are twisted together, that they acquire any appreciable degree of strength. Linen, on the other hand, consists of woody tissue, in the shape of long thick-sided tubes, adhering in bundles, the articulations being always oblique, and the ends of the tubes pointed and overlying each other; moreover, the individual tubes are much stronger than those of cotton. In short, cotton is a development of the parenchymatous tissue, which is the weakest among the elementary organs of a plant; linen, of the woody tissue, which is the strongest: hence the well-known superiority of linen to cotton in strength.

Cotton fibre consists of nearly pure cellulose associated with only 1 to 1½ per cent. of inorganic matter. The following table exhibits the composition of cotton (after deduction of the ash), as compared with that of pure cellulose  $C^6H^{10}O^4$ .

#### Analyses of Cotton.

	Gladstone.	Ransome.	Schmidt and Hecker.	Petten- kofer.	Calculation.
Carbon . . . .	44.37	44.20	43.27	44.5	C <sup>6</sup> . . . 44.44
Hydrogen . . .	7.24	7.04	6.30	6.1	H <sup>10</sup> . . . 6.17
Oxygen . . . .	48.39	48.76	50.43	49.4	O <sup>4</sup> . . . 49.39
	100.00	100.00	100.00	100.00	100.00

Cotton (and linen) may be distinguished from silk and wool by their behaviour with sulphuric acid and with nitric acids. Silk and wool are turned yellow by immersion in strong nitric acid, whereas cotton and linen remain colourless. When woollen tissues containing cotton or linen are immersed for a quarter of an hour in sulphuric acid, the cotton and linen first swell to a pasty mass, and afterwards dissolve, while the animal fibres remain unaltered. (Böttger, J. pr. Chem. lxxiii. 498.)

Cotton dissolves in sulphuric acid more quickly than linen; hence it may be detected

in linen by the following method. The tissue, after being repeatedly washed with rain-water, boiled with water, and dried, is dipped for  $\frac{1}{2}$  to 2 minutes in oil of vitriol, then carefully pressed under water with the fingers, washed with water, immersed for a few seconds in aqueous ammonia, carbonate of potassium, or carbonate of sodium, again washed with water, and dried between filtering paper. By this treatment, the cotton fibres are dissolved, while the linen fibres are merely rendered thinner and more translucent, according to the duration of the experiment; after a short immersion the cotton fibres appear transparent, while the linen fibres remain white and opaque.

Another distinction between cotton and linen is that the latter acquires a deep yellow colour by boiling with water containing its own weight of hydrate of potassium, whereas cotton is little or not at all coloured by the same treatment. (Gm. xv. 140.)

Cotton cloth (calico), immersed for 10—30 minutes in syrupy *potash-ley*, and then washed with alcohol of specific gravity 0.825, contracts by  $\frac{1}{10}$  after drying, and contains 14.72 per cent. potash, corresponding to the formula  $4C^6H^{10}O^5.K^2O$  which requires 14.59 per cent.  $K^2O$  (Gladstone, Chem. Soc. Qu. J. v. 17). Calico immersed in *soda-ley* of specific gravity 1.342 and treated in a similar manner, shrinks in drying by  $\frac{1}{10}$ , and contains 9.68 per cent. soda ( $4C^6H^{10}O^5.Na^2O = 9.65$  per cent.). Unwoven cotton forms a similar compound; longer immersion or the use of a stronger solution appears to produce partial solution and decomposition. Cotton also unites with soda in other proportions, but never with a larger quantity than that contained in the compound just mentioned. Water abstracts all the soda from the compounds, and leaves a shrunken tissue which takes more brilliant colours in dyeing than ordinary calico. (Gladstone, *loc. cit.* See also Mercer. Rep. Pat. Inv. 1851, p. 358; Gm. xv. 141.)

Cotton immersed in solutions of *alum* or *acetate of aluminium*, does not separate any alumina; but if the solution of acetate of aluminium, ferric acetate, or any other salt containing a volatile acid be left to dry on the cotton, the acid volatilises after a while, and the base is so firmly fixed on the cotton, though only mechanically, that it cannot be removed by washing with water (Walter Crum, Ann. Ch. Pharm. lv. 223, Compt. rend. xlvii. 961). If the cloth after this treatment be immersed in a coloured solution, such as that of logwood or indigo, the colouring matter forms an insoluble compound with the base, and thus becomes permanently fixed upon the cotton fibre; whereas, if the cloth were merely dipped in the coloured infusion without being previously treated with the metallic salt, or *mordant*, the colour imparted to it would be immediately removed by immersion in water: cotton, flax, hemp, and other vegetable fibres do not, like wool and silk, exert any specific attractive power on the colouring matters mixed with mordants. (See DYEING.)

*Culture of Cotton*.—Professor Mallet of Alabama has lately published the commencement of an elaborate investigation of the chemical and physical conditions of the cultivation of cotton (Proc. Roy. Soc. xi. 340), from which the following general conclusions are drawn.

The annual cotton plant, as cultivated in America, attains its principal growth during four months, though it continues to develop seed and fibre for a much longer period.

It requires a very finely divided soil through which its rootlets can penetrate with facility; the average mass of soil interpenetrated by the roots of each plant is about 5 cubic feet.

Cotton is not an exhaustive crop, inasmuch as the great mass of the plant—root, stem, branches, leaves, and emptied bolls—remains upon the field and is ploughed into the soil, and nothing is removed but the fibre and the seed; and the greater part of the latter is also returned to the soil, the seed being thickly strewn by handfulls in a continuous row, from which the plants are afterwards thinned. The cotton fibre, which constitutes the salable product, and is absolutely carried off the land, may be looked upon as a very light crop; a bale of 400 to 500 lbs to the acre is sometimes obtained under favourable circumstances, but this is much above the average for upland cotton. The fibre yields from 1 to 1.5 per cent. of ash, so that at the most,  $7\frac{1}{2}$  lbs. of mineral matter will be removed annually, which is not half as much as is removed by a crop of wheat of 25 bushels to the acre in the *grain alone*, and less than  $\frac{1}{10}$  the amount removed by an average crop of potatoes. Sometimes, however, a considerable portion of the seed is removed from the plantation to be used for the extraction of oil, the cake which remains being exported to Europe for cattle-food. This practice tends greatly to the exhaustion of the cotton soil.

Cotton is decidedly a *sun-plant*, requiring a high summer temperature and plenty of sunshine. A moderate supply of rain is advantageous in the early stage of growth, but heavy rains are injurious even in that stage, and later in the season they are absolutely destructive. A water-soaked soil is decidedly unfavourable, the tap-root not striking down in such soil, and the plant looking small and sickly, and bearing but little cotton. The soil most favourable for cotton cultivation is a finely divided soil capable of absorbing a considerable quantity of aqueous vapour from the atmosphere and retaining it in a state of adhesion or of chemical combination, so as not to render



the soil moist to the touch. Such a soil enables the plant to withstand vicissitudes of weather and season, storing up hygroscopic moisture in damp seasons, and yielding a gradual supply of it to the roots in the latter stage of the growth when seed and fibre are forming. Another essential condition of the soil is the power of gradually absorbing and yielding a considerable quantity of gases, especially ammonia, and of mineral matter withdrawn from solution.

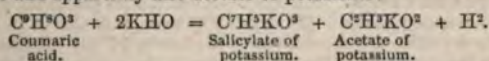
All these conditions are fulfilled in a high degree by the soil of the prairie region of Central Alabama, which is a stiff aluminous clay, containing a moderate amount of organic matter and of the mineral substances needed by the plant as food—of great uniformity, and in an exceedingly fine state of division; above all, possessing a very high capacity for absorbing and retaining heat, moisture, gases, and soluble mineral matter. It was found to be capable of condensing 52 times its own volume of ammonia gas, and the subsoil, which is calcareous, was found to absorb 64 times its own volume of the same gas.

**COTUNNITE.** Native chloride of lead,  $PbCl$ , found in the crater of Vesuvius after the eruption of 1822, in acicular crystals of the trimetric system, and capillary masses, white, having a strong lustre, of specific gravity 5.238, and soft enough to be scratched by the nail.

**COUMARAMINE.**  $C^9H^7NO^2 = N.H^2.C^9H^5O^2$ .—Produced by the action of ferrous acetate (iron filings and dilute acetic acid) on nitrocoumarin. The reaction must be continued for twenty-four hours, and the filtrate concentrated by evaporation; it then, on cooling, deposits coumarin in fine yellowish needles, often several centimetres long. It is nearly insoluble in cold water and in ether, but dissolves readily in boiling water or alcohol. A saturated solution of ferrous acetate appears to dissolve it more readily than cold water. It melts between  $168^\circ$  and  $170^\circ C$ , and if cautiously raised to a higher temperature, sublimes without decomposition in pale yellow scales. It is rapidly decomposed by boiling potash; the liquid saturated with an acid deposits brown flakes.

Coumaramine unites with acids, forming soluble salts, from which ammonia precipitates the base in a crystalline mass. The hydrochlorate forms scales very soluble in water. The chloroplatinate,  $C^9H^7NO^2.HCl.PtCl^2$ , is a yellow crystalline precipitate insoluble in water. (Chiozza and Frapelli, *Ann. Ch. Pharm.* xcv. 252.)

**COUMARIC ACID.**  $C^9H^7O^3 = C^9H^5O^2.HO$  = coumarin + 1 at. water. (Delalande, *Ann. Ch. Phys.* [3] vi. 343.—Bleibtreu, *Ann. Ch. Pharm.* lix. 177.)—Prepared by boiling coumarin with strong potash-ley, adding solid potash if necessary, and precipitating by hydrochloric acid. Crystallises in colourless brilliant laminae, having a bitter taste, and soluble in water, alcohol, and ether. It melts at  $190^\circ C$ , and at a higher temperature decomposes partially, yielding a crystalline sublimate, and leaving a brown residue. By distillation it yields an oil, which reddens ferric salts and appears to unite with potash. Coumaric acid, when pure, does not impart any violet colour to ferric salts. When melted with potash it gives off hydrogen, and yields salicylate and apparently also acetate of potassium:



Coumaric acid decomposes carbonates. The formula of the coumarates is  $C^9H^7O^2.M$ . Coumarate of ammonium does not precipitate barium-salts. Coumarate of lead is a white precipitate, pulverulent, and insoluble in water. Coumarate of silver is a light yellow pulverulent precipitate, or if formed in presence of ammonia, orange-coloured and flocculent.

**COUMARIN.**  $C^9H^6O^2$  or  $C^9H^5O^2$ . (Guibourt, *Histoire des Drogues simples*.—Boullay and Boudron-Chaillard, *J. Pharm.* xi. 480.—Delalande, *Ann. Ch. Phys.* [3] vi. 343.—Bleibtreu, *Ann. Ch. Pharm.* lix. 177.—Gm. xiii. 321.)—This substance exists in considerable quantity in Tonka beans, the fruit of *Coumaruma odorata*, or *Dipteryx odorata*, being found in small white crystals between the seed coating and the kernel. It is also found in woodruff (*Asperula odorata*), in *Melilotus officinalis*, in the flowers of sweet-scented vernal grass (*Anthoxanthum odoratum*), in the leaves of *Faham*, an orchidaceous plant (*Angraecum fragrans*), in the leaves of *Orchis fusca* (Bley), and in the dried leaves of *Liastris odoratissima*, a composite plant growing in the southern parts of North America (Procter, *Rép. Chim. app.* 1861, p. 143). In some of these plants, the coumarin was originally mistaken for benzoic acid.

Coumarin is easily extracted from Tonka beans by digesting them in strong alcohol. On evaporating the alcohol, a crystalline magma of coumarin is obtained, which may be decolorised and freed from a quantity of adhering oil by means of animal charcoal.

Coumarin is colourless; it crystallises sometimes in small rectangular plates, some-

times in large prisms belonging to the trimetric system,  $\infty P : P \infty$ , with  $\infty P \infty$  predominant. Inclination of the faces  $\infty P \infty : P \infty = 100^\circ$  (nearly),  $\infty P : P \infty = 104.5$  (nearly),  $a : b : c = 0.364 : 1 : 1.035$ . It melts at  $50^\circ C$ , and boils at  $270^\circ$  without sensible alteration; has an agreeable aromatic odour, and a burning taste; the vapour acts very strongly on the brain.

Coumarin is nearly insoluble in cold water, but boiling water dissolves it abundantly, and deposits it on cooling in very slender needles. It dissolves without alteration in dilute acids. Strong sulphuric acid chars it immediately. Strong nitric acid converts it into nitrocoumarin, and, after long boiling, into picric acid. Heated with excess of potash, it yields salicylic acid and coumaric acid,  $C^9H^9O^3$ . Chlorine and bromine form crystalline compounds with coumarin; iodine converts it into a bronze-green crystalline substance. With pentachloride of antimony, coumarin forms a crystalline compound containing  $C^9H^9O^3.SbCl^5$ .

**Nitrocoumarin.**  $C^9H^5(NO^3)O^3$ .—Obtained by projecting coumarin by small portions at a time into cold fuming nitric acid, and precipitating with a large quantity of water. It is then deposited as a snow-white flocculent mass. It dissolves in boiling water, alcohol, and ether, and crystallises from the solution in small white silky needles. Melts at  $170^\circ C$ , and sublimes undecomposed at a high temperature in nacreous crystals. Potash colours it deep red and dissolves it. Acids added to the solution throw down unaltered nitrocoumarin. It dissolves in ammonia; the solution when boiled evolves ammonia, and on cooling deposits part of the nitrocoumarin in white crystals, not containing ammonia (Bleibtreu). Ferrous acetate converts nitrocoumarin into coumaramine. (Frapolli and Chiozza, p. 194.)

The ammoniacal solution of nitrocoumarin, freed from excess of ammonia by boiling, and filtered, forms, with acetate of lead, an orange-yellow precipitate,  $2C^9H^5(NO^3)O^3.3Pb^2O$ , soluble in a large quantity of water, less soluble in alcohol, insoluble in ether, decomposed by acids. With nitrate of silver, in like manner, a beautiful orange-coloured precipitate,  $C^9H^5(NO^3)O^3.Ag^2O$ , is obtained, which explodes when heated. (Bleibtreu.)

**COURBARIL RESIN.** A name sometimes given to West Indian animé resin, obtained from the *Hymenæa Courbaril*. (See i. 296.)

**COUZERANITE.** A silicate found in the neighbourhood of Couzeran in the Pyrenees. It contains 52.37 per cent.  $SiO^2$ , 24.02  $Al^2O^3$ , 11.85  $Ca^2O$ , 1.40  $Mg^2O$ , 5.52  $K^2O$ , and 3.96  $Na^2O$  (Dufrenoy), which is nearly the composition of dipyre (*q. v.*) According to Dufrenoy, the crystals belong to the monoclinic system, whence he refers it to Labradorite; but, according to R. P. Grey, jun., they are dimetric, like those of dipyre, which mineral is also found in the same locality. Specific gravity = 2.69. Hardness = 6.0, or rather above. Colour black to grey. Lustre waxy. Opaque. Melts to a white enamel before the blowpipe. Insoluble in acids. (Handw. d. Chem. ii. [3] 220.—Dana, ii. 206.)

**COVELLIN.** Native protosulphide of Copper. See COPPER, SULPHIDES OF (ii. 74).

**CRAITONITE.** See CRICHTONITE.

**CRAMBE MARITIMA.** See Kale.—A cruciferous plant, the young sprouts of which contain, according to T. J. Herapath (Chem. Soc. Qu. J. ii. 4), in the fresh state 0.71, in the dry state 9.9 per cent. ash; the leaves 1.7 per cent. in the fresh, and 16.7 per cent. in the dry state. The composition of the ash is as follows:—

		$CO^2$	$SO^3$	$P^2O^3$	$K^2O$	$Na^2O$	$NaCl$
Soluble in water	{ Sprouts	4.2	21.8	5.1	6.7	23.6	trace
	{ Leaves	6.9	15.1	trace	2.1	20.8	12.1
		$Ca^2CO^3$	$Mg^2O^3$	$Ca^2SO^4$	$Ca^2PO^4$	$Mg^2PO^4$	Ferric phosphate, Silica.
Insoluble in water	{ Sprouts	3.6	trace	trace	30.7	trace	trace 4.2
	{ Leaves	27.2	trace	1.5	13.1	trace	1.6 0.1

**CRATEGIN.** A non-azotised bitter principle, obtained from the fresh branch-bark of the white-thorn (*Crataegus oxyacantha*). It crystallises in greyish-white nodules, like grape-sugar, has a bitter taste, dissolves easily in water, less easily in alcohol, not at all in ether, and does not combine either with acids or with alkalis. (Leroy, J. Chim. Méd. xvii. 3.)

**CRATININE.** Gmelin's name for CREATININE (*q. v.*)

**CRAURITE.** See DUFREYNITE.

**CREAM.** The fatty portion of milk, which rises to the surface when fresh milk is left at rest for twenty-four hours. Berzelius found in 100 pts. of cream from cow's milk, 4.5 pts. of butter, 3.5 casein, and 92.0 serum.

**CREAM OF TARTAR.** Acid tartrate of potassium (see TARTARIC ACID).



**CREATINE.**  $C_4H_7N_3O_2$ , or  $C_4H_9N_3O_4$ . (Chevreul, J. Pharm. xxi. 234; Pettenkofer, Ann. Ch. Pharm. lii. 97; Liebig, Ann. Ch. Pharm. lxii. 282; Heintz, Pogg. Ann. lxiii. 602; lxx. 460; lxxiii. 696; lxxiv. 126; Compt. rend. xxiv. 500; Gregory, Chem. Soc. Qu. J. i. 25; Dessaignes, Compt. rend. xxxviii. 839; xli. 1258; Ann. Ch. Pharm. xvii. 339; J. Pharm. [3] xxxii. 41; Gm. x. 249; Gerh. i. 530; iii. 939; iv. 893.)—An organic base discovered in 1835 by Chevreul in the juice of flesh; more minutely examined by Liebig in 1847.

*Sources.*—In the muscular flesh of mammalia, birds, amphibia, and fishes. Lean horse-flesh contains 0.070, and the flesh of poultry 0.35 per cent. of creatine. That of the marten yields less than that of poultry, but more than that of other quadrupeds: after horse-flesh follow, in decreasing series, the flesh of the fox, roe-buck, stag, hare, ox, sheep, pig, calf, and pike. Fat animals yield much less creatine than lean ones; e. g. a fox fattened on meat for 100 days, yields only  $\frac{1}{10}$  as much as one that has been killed in the chase (Liebig). Bullock's heart yields 0.142; the flesh of poultry 0.321; that of the pigeon 0.083, that of cod 0.170; and that of the ray 0.61 per cent. (Gregory). Human flesh yields 0.067 per cent.; that of the alligator likewise contains creatine (Schlossberger, Ann. Ch. Pharm. lxvi. 80; xlix. 344). The flesh of the Borqual whale (*Balenoptera musculus*) likewise yields a small quantity of creatine. (D. Price, Chem. Soc. Qu. J. iii. 229.)

Städeler, has obtained creatine from the flesh of the dog, pigeon, *Spinax acanthus*, and *Petromyzon fluviatilis* (J. pr. Chem. lxxii. 256). Creatine is likewise found, together with creatinine, in urine; together with creatinine and seroline in blood (Verdeil and Marcet, J. Pharm. [3] xx. 89); and, together with urea, in the brain of pigeons and of dogs. (Städeler.)

It is not yet decided whether creatine exists, as such, in the living animal body, or whether it is formed from creatinine existing therein, by the process of preparation. Creatine and creatinine differ in composition only by the elements of water, and are easily converted one into the other,—creatine into creatinine under the influence of acids, creatinine into creatine, by the action of alkalis, the action in either case being accelerated by heat. Now, in preparing creatine either from flesh-juice or from urine, the usual process is to neutralise with an alkali, and concentrate the liquid by heat; by this process the creatinine existing in the original liquid is sure to be converted partly, if not wholly, into creatine, and it is possible that the whole of the creatine actually obtained may be produced in this way; for there is no simple reaction by which creatine can be detected in the original liquid, in presence of creatinine. From the experiments of Dessaignes (J. Pharm. [3] xxxii. 41), it appears that human urine yields more creatinine and less creatine the more quickly the process of separation is conducted. Liebig (Ann. Ch. Pharm. cviii. 334) found that the fresh urine of a dog which had been fed on meat for some weeks, yielded, when mixed with milk of lime and immediately evaporated, a considerable quantity of creatinine but no creatine, but if left to stand for six weeks before evaporation, it yielded creatine without creatinine. In this case the creatine evidently resulted from the decomposition of the creatinine. Dessaignes is of opinion that the creatine of muscular flesh is likewise produced by the decomposition of creatinine.

*Preparation.* 1. *From muscular flesh.*—a. The aqueous extract of beef is evaporated in vacuo; the residue exhausted with alcohol, and the alcohol evaporated till the creatine crystallises out. The greater portion remains, however, in the mother-liquor, being prevented from crystallising by the presence of foreign bodies (Chevreul). In a similar manner, Schlossberger obtained creatine from the flesh of the alligator and purified the crystals by washing with cold alcohol.

b. The fresh lean muscular flesh of mammalia or birds, is freed as much as possible from fat (which would stop up the press-bag when the meat is subjected to pressure), and chopped up fine; 5 lbs. of it are then well kneaded with an equal weight of water; the liquid is well pressed out in a coarse linen bag; the residue twice treated with water in a similar manner; 5 lbs. of muscular flesh kneaded together with the expressed liquid; the residue kneaded with the third expressed liquid, and then after pressure with 5 lbs. of pure water; and the united liquids are strained through a cloth. The resulting reddish liquid, which reddens litmus, is kept at 100° C., in a large glass flask over the water-bath, till the albumin and blood-red have completely separated in the form of a coagulum, and a sample of the liquid remains clear when boiled.

To decolorise the liquid obtained from some kinds of meat, it must be heated in a basin till it froths up. The liquid is then strained, first through linen, the coagulum being pressed out, then through paper.\* The filtrate is then mixed with saturated

\* The filtrate obtained from the flesh of the ox, roebuck, hare, or fox, which contains a large quantity of blood, retains a reddish tint; that from real, poultry, or pike is nearly colourless; game and poultry yield a nearly transparent filtrate, which is very favourable to the obtaining of creatine; horse-flesh and cod yield a turbid filtrate. If the filtrate were evaporated alone, even below 100°, it would become coloured

baryta-water, the addition of that liquid being continued, even after the filtrate has been rendered neutral or alkaline by it, as long as a precipitate of phosphate of barium and phosphate of magnesium continues to form; the filtrate evaporated in a shallow basin over the water-bath to  $\frac{1}{10}$ ; and the thickish residue set aside, first in a warm place to evaporate further, and then, after crystallisation has commenced, in the cold.\* The needles thus obtained are separated from the mother-liquor by filtration, washed first with water, then with alcohol, and dissolved in boiling water; and the solution, if coloured, digested with a small quantity of blood-charcoal, then filtered and left to cool, whereupon it yields pure crystals of creatine (Liebig). If a sufficient quantity of baryta-water has not been added, the crystals will be contaminated with phosphate of magnesium. In that case, the hot aqueous solution must be boiled with a small quantity of hydrated oxide of lead; digested, after filtration, with blood-charcoal, which removes the last traces of lead; and the filtrate again left to crystallise. (Liebig.)

c. The chopped flesh of pike, when boiled with water, swells up to a gummy mass, from which the liquid cannot be expressed. A mixture of the chopped flesh with water must therefore be thrown upon a funnel; small quantities of water allowed to run gradually through; and the slightly turbid, acid liquid, which smells and tastes of fish, separated from the soft, white coagulum, precipitated with baryta-water, then filtered and evaporated. It forms on cooling a colourless jelly, in which, in the course of 24 hours, crystals of creatine begin to form. (Liebig.)

The extract of the flesh of poultry or pigeons deposits brown flakes, together with the creatine crystals;—the flesh of bullock's heart often yields but few of the purer crystals, but a considerable quantity of brown flakes, from which boiling water extracts a large additional quantity of creatine. From skate and cod the juice may be easily expressed, after the flesh has been mixed with rather more than equal quantity of water; the jelly ultimately obtained from it, in which the creatine-crystals form, dissolves readily in cold water, and deposits more crystals: the flesh of cod yields the whitest creatine. From the syrupy mother-liquors of crude creatine, chloride of zinc does not form any zincochloride of creatinine, or only a trace; but the mother-liquors obtained in the recrystallisation of crude creatine yield this precipitate on addition of chloride of zinc. (Gregory.)

d. Chopped flesh mixed with coarsely pounded glass, is digested with  $1\frac{1}{2}$  times its volume of alcohol at a gentle heat; the liquid is then pressed out and distilled; the residue treated with basic acetate of lead, the excess of lead separated by sulphydric acid, and the clear liquid evaporated to a syrup. On cooling, creatine crystallises out; and after some days the crystalline mass is spread out on unsized paper to absorb the mother-liquor; after which the creatine is dissolved in hot water or alcohol, and recrystallised. (Städeler, J. pr. Chem. lxxii. 256.)

2. From Zinc-chloride of Creatinine.—a. The solution of this compound in boiling water is digested with hydrated oxide of lead, till it acquires a strong alkaline reaction; filtered from the oxide of zinc and oxychloride of lead; digested with a little blood-charcoal, which removes the small remaining quantity of lead, together with fibrin; the filtrate evaporated to dryness; and the remaining mixture of creatine and creatinine, treated with an eightfold quantity of boiling alcohol to dissolve out the latter: the alcohol, on cooling, likewise deposits crystals of creatine, which are added to the undissolved residue of creatine, and the whole is purified by recrystallisation. (The alcohol filtered after cooling deposits creatinine; Liebig.)—b. The boiling aqueous solution of the zinc-compound is treated with baryta-water, which precipitates zinc-oxide, together with the greater part of the adhering fibrin; carbonic acid gas is passed through the filtrate; the liquid again filtered to separate carbonate of barium; the filtrate evaporated to dryness in vacuo; the residue exhausted with alcohol; the baryta which has been taken up by the alcohol as chloride of barium, precipitated by sulphuric acid; the liquid again filtered, boiled with oxide of lead, treated with absolute alcohol to precipitate all the chloride of lead, and filtered from chloride and sulphate of lead; any lead that may yet remain dissolved is removed by sulphuretted hydrogen; and the filtrate is evaporated to dryness over the water-bath (Pettenkofer). The residue thus obtained contains creatinine as well as creatine (Liebig).—c. The boiling aqueous solution of the zinc-compound is mixed with ammonia till it begins to

in consequence of the presence of free acid, which would decompose the creatine, and leave a dark-brown syrup, having the odour of roast meat, which would yield but a very small quantity of creatine, even after long standing. This appears to be the reason why Berzelius (Jahresber. viii. 589) and Fr. Simon (N. Br. Arch. xxvi. 283) did not succeed in preparing creatine.

\* The filtrate from poultry remains clear when evaporated, and becomes covered with a film of carbonate of barium if too much baryta-water has been added; that from beef becomes covered, when concentrated to a thin syrup, with a mucous scum which swells up in water, but is insoluble and must be removed; and that from veal or horse-flesh with films which are continually renewed, and must be continually skimmed off.



show turbidity, and then precipitated with sulphide of ammonium; the filtrate evaporated to a small bulk, and mixed with absolute alcohol; and the crystals of creatine, which separate from the liquid after long standing in the cold, are purified by recrystallisation from water (Heintz). The creatinine remains in the alcoholic mother-liquor.

The crystals of creatine obtained by either of these processes may be freed from water of crystallisation by heating them to 100° C. (Liebig.)

*Properties.*—Anhydrous creatine forms a white opaque mass (Liebig). It is inodorous, has a somewhat bitter taste, and produces a scratching sensation in the throat (Liebig). Neutral to vegetable colours. (Chevreul.)

The composition of creatine dried at 100° C. is as follows:—

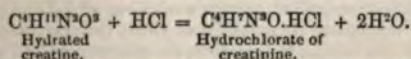
Calculation.				Analyses.		
				Liebig. <i>a.</i>	Liebig. <i>b.</i>	Heintz. <i>c.</i>
C <sup>4</sup>	. . . 48	36.64		36.66	36.90	36.39
H <sup>9</sup>	. . . 9	6.87		6.96	7.07	6.86
N <sup>3</sup>	. . . 42	32.06		32.15	32.61	31.64
O <sup>2</sup>	. . . 32	24.43		24.23	23.42	25.11
C <sup>4</sup> H <sup>9</sup> N <sup>3</sup> O <sup>2</sup>	. 131	100.00		100.00	100.00	100.00

*a* was obtained from meat; *b*, from zinc-chloride of creatinine prepared from human urine.

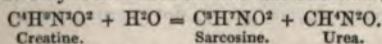
The *hydrate*, C<sup>4</sup>H<sup>9</sup>N<sup>3</sup>O<sup>2</sup>.H<sup>2</sup>O, forms perfectly limpid prisms, belonging to the monoclinic system. Inclination of the clinodiagonal to the principal axis = 70° 20'. Inclination of the faces ∞P: ∞P in the plane of the orthodiagonal and principal axis = 133° 2' (nearly). Specific gravity of the crystals = 1.35 to 1.34.

Creatine dissolves in 7.46 pts. of water at 18° C.; it is very soluble in boiling water and is deposited on cooling in a mass of needles. It dissolves in 9410 pts. of absolute alcohol, but is more soluble in aqueous alcohol; insoluble in ether.

*Decompositions.*—1. Hydrated creatine, when heated, first gives off its water of crystallisation with decrepitation; then melts without becoming coloured; afterwards emits an odour of ammonia, hydrocyanic acid, and phosphorus; and lastly, gives off yellow fumes, which condense partly to an oil, partly to needle-shaped crystals, and leaves a small quantity of charcoal (Chevreul).—2. The solution of creatine in aqueous hypermanganate of potassium is decolorised by continued digestion, without evolution of gas, the creatine being decomposed and carbonate of potassium formed (Liebig). The aqueous solution of creatine is not decomposed by boiling with peroxide of lead (Liebig). It is not coloured by boiling with mercuric nitrate (Chevreul).—3. Creatine dissolved in strong nitric, sulphuric, phosphoric, or hydrochloric acid, is converted into creatinine by abstraction of H<sup>2</sup>O, the creatinine then combining with the acid (Liebig). But if these acids are dilute, the creatine remains unaltered, even after long boiling, and the solution in cold hydrochloric acid leaves, by spontaneous evaporation, crystals of pure creatine (Liebig). If dry hydrochloric acid gas be passed over 149 pts. (1 at.) of hydrated creatine heated to 100° C., the weight first increases by absorption of hydrochloric acid; but if dry air be then passed through the apparatus for some time, water is continuously given off, and the compound diminishes in weight, till it amounts to only 154.16 pts., and contains 38.05 pts. (a little more than 1 at.) hydrochloric acid. Hence 36 pts. (1 at. of water of crystallisation and 1 at. more produced from the creatine) have been given off, and on the other hand, 38.05 pts. (1 at.) hydrochloric acid have entered into combination with the hydrated creatine:

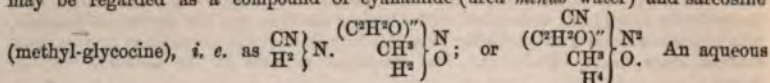


131 pts. (1 at.) of dry creatine, similarly treated with hydrochloric acid gas, take up about 18.04 pts., because, in this case, only 18 pts. (1 at.) water are given off for every 36.4 pts. (1 at.) hydrochloric acid taken up (Liebig).—The colourless solution of creatine in nitric acid of specific gravity 1.34 gives off nitrous fumes when heated in the water-bath, and leaves on evaporation a colourless residue (of nitrate of creatinine), which dissolves in water, separates out therefrom in small granules, and does not precipitate dichloride of platinum (Chevreul).—4. By boiling with a small quantity of baryta dissolved in water, creatine is resolved into sarcosine and urea, which is then quickly resolved by the baryta into carbonic acid and ammonia (Liebig):

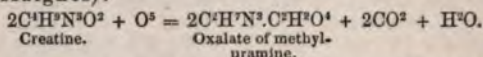


From this decomposition Strecker (Ann. Ch. Pharm. cxviii. 151) infers that creatine

may be regarded as a compound of cyanamide (urea *minus* water) and sarcosine



solution of creatine saturated at the boiling heat, and mixed with crystals of baryta amounting to 10 times the weight of the creatine, remains clear at first, but, if the boiling be continued, gives off abundance of ammonia; deposits carbonate of barium at the same time; and, if fresh baryta be added from time to time, is ultimately found to contain scarcely any thing but sarcosine and carbonate of barium; and, if the operation be interrupted during the strongest evolution of ammonia, likewise a little urea. A small quantity of another substance, probably urethane, is however produced at the same time: for if the alcohol from which the sulphate of sarcosine has crystallised out, be mixed with water, neutralised with carbonate of barium, filtered and evaporated to a thin syrup, colourless needles and laminæ are obtained which reddened litmus very slightly, fuse and volatilise when heated, without leaving baryta, and dissolve in water, in alcohol, and in 30 pts. of ether; their aqueous solution does not precipitate the salts of barium, calcium, or silver, or neutral acetate of lead, or corrosive sublimate (Liebig).—5. The aqueous solution becomes turbid by long standing (if, according to Liebig, it contains a trace of foreign organic matter), and evolves a sickening ammoniacal odour (Chevreul).—6. When *nitrous gas* is passed into a solution of creatine in nitric acid, an alkali is formed, having the composition  $\text{C}^3\text{NH}^3$  (Dessaigues).—7. When an aqueous solution of creatine is heated with *mercuric oxide*, carbonic acid is evolved, and methyluramine ( $\text{C}^3\text{H}^3\text{N}^2$ ) obtained in the form of an oxalate (Dessaigues):



The same transformation is effected by a mixture of peroxide of lead and sulphuric acid (Dessaigues).—8. Hot *nitric acid* decomposes creatine, yielding methylamine and ammonia (Dessaigues).—9. Creatine heated with *soda-lime*, gives off methylamine. (Dessaigues.)

**SALTS OF CREATINE.** Creatine is a very weak base, not being capable of neutralising the weakest acids, even when added in very large quantity. (Liebig.)

*Sulphate of Creatine*,  $2\text{C}^3\text{H}^3\text{N}^2\text{O}^2 \cdot \text{SO}^4\text{H}^2$ , and the *Hydrochlorate*,  $\text{C}^3\text{H}^3\text{N}^2\text{O}^2 \cdot \text{HCl}$ , are obtained in fine prisms by dissolving creatine in the proper quantity of acid, and evaporating the solution at  $30^\circ \text{C}$ . or in vacuo; they are soluble in water but not deliquescent. (Dessaigues.)

*Nitrate of Creatine*,  $\text{C}^3\text{H}^3\text{N}^2\text{O}^2 \cdot \text{NO}^3\text{H}$ .—Obtained by dissolving crystallised creatine in the requisite quantity of nitric acid, and evaporating the solution at  $30^\circ \text{C}$ .; or by passing a rapid stream of nitrous gas through water containing an excess of creatine in suspension. The creatine dissolves with tolerable rapidity, and a considerable quantity of small shining crystals of the nitrate are formed, which, when recrystallised by dissolving them in lukewarm water and cooling, form thick short prisms. This salt is less soluble in water than the sulphate or hydrochlorate. The solution has a very sour taste, and is decomposed by ammonia with precipitation of creatine. (Dessaigues.)

From a solution in warm baryta-water, creatine crystallises on cooling without taking up any baryta. (Liebig.)

The aqueous solution of creatine does not precipitate chloride of barium, basic acetate of lead, ferric sulphate, cupric sulphate, nitrate of silver, or dichloride of platinum (Chevreul). It does not precipitate chloride of zinc, unless it contains creatinine (Heintz). The warm non-boiling, aqueous solution, added to chloride of zinc, does not throw down any crystalline compound, but yields the creatine in the separate state on cooling (Liebig). On boiling the mixture, the zinc-precipitate is formed (Heintz), probably from conversion of the creatine into creatinine.

**CREATININE**,  $\text{C}^3\text{H}^3\text{N}^3\text{O}$  or  $\text{C}^3\text{H}^3\text{N}^3\text{O}^2$ . (Liebig, Ann. Ch. Pharm. lxii. 298 and 324.—Heintz, Pogg. Ann. lxii. 602; lxxiii. 595; lxxiv. 125.)—Heintz and Pettenkofer, in 1844, and nearly at the same time, discovered in human urine a nitrogenous substance which formed a crystalline precipitate with chloride of zinc. The crystalline substance separated from this precipitate was regarded by Pettenkofer as a peculiar compound =  $\text{C}^3\text{H}^3\text{N}^3\text{O}^3$  [plainly a mixture of creatine and creatinine], by Heintz, at first as an acid, and afterwards as creatine, till Liebig, in 1847, showed that it was a mixture of creatine and creatinine, which latter he had just before discovered and investigated, having obtained it by decomposing creatine with concentrated acids.

*Sources*.—1. In human urine, to the amount of 0.5 per cent. (Pettenkofer), and,



according to Heintz, likewise in the urine of horses and other mammalia. Socoloff has found it in the urine of horses and of calves.—2. In muscular flesh. As it occurs in the mother-liquor of the creatine prepared from flesh, and as dilute acids do not convert creatine into creatinine, we cannot suppose that this creatinine of muscular flesh is formed by heating the decoction of the flesh (Liebig, see p. 97).—3. In blood. (Verdeil and Marcet.)

*Formation.*—From creatine, by the action of the stronger mineral acids.

*Preparation*—1. *From Human urine.*—*a.* Fresh human urine is neutralised with carbonate of sodium, and evaporated below  $100^{\circ}$  C. to a syrup (till the salts crystallise out, according to Liebig); this syrup is exhausted with alcohol; the filtrate mixed with a concentrated solution (alcoholic, according to Heintz) of chloride of zinc, which at first throws down a brown amorphous precipitate, containing zinc (phosphate of zinc, according to Heintz), then after several hours, crystalline grains; the whole of the precipitate, after standing for some time is collected on a filter (Heintz washes it with weak alcohol); boiled with water, which leaves the amorphous precipitate undissolved; and the filtrate evaporated,—whereupon it yields yellow crystals, which may be freed from adhering salts by repeated boiling with strong alcohol (Pettenkofer).—*b.* Fresh human urine is neutralised with milk of lime; chloride of calcium added as long as a precipitate of phosphate of calcium continues to form; the filtrate evaporated till the salts crystallise out; 32 pts. of the mother-liquor mixed with 1 pt. of chloride of zinc dissolved in the smallest possible quantity of water; the mixture set aside for four days; and the zinc-compound which separates in nodules washed with cold water (Liebig).—*c.* Putrid human urine is boiled with excess of milk of lime till it no longer gives off ammonia; the filtrate is evaporated to a syrup, and mixed as above with chloride of zinc; and the crystals which form after long standing, are washed. (Liebig; see also Dessaignes, J. Pharm. [3] xxxii. 42.)

To purify the crystals, it is not good to use bone-charcoal, which occasions great loss;—but they must be dissolved in hot water; the solution mixed with ammonia till a precipitation begins to form; the precipitation completed by means of sulphide of ammonium; the filtrate highly concentrated and mixed with absolute alcohol; the nearly white crystals of creatine and creatinine, which are obtained by cooling the solution to a low temperature, dissolved in the smallest possible quantity of boiling water; the solution mixed with alcoholic chloride of zinc; and the precipitate, which forms on setting the liquid aside in a cold place, washed with alcohol. The above-mentioned mother-liquor of creatine, which likewise contains sal-ammoniac, also yields, with alcoholic chloride of zinc, a precipitate which, when purified by crystallisation from boiling water, yields the zinc-compound in white crystals. (Heintz; see also Löbe, J. pr. Chem. lxxxii. 170; Rép. Chim. pour 1861, p. 25.)

The zinc-compound is then decomposed with hydrate of lead in the manner described at page 96, and the mixture of creatine and creatinine thus obtained, is digested in the cold with very strong alcohol, which dissolves the creatinine and leaves the creatine: great care must be taken to avoid rise of temperature, otherwise some of the creatine will also be dissolved. (Neubauer, Ann. Ch. Pharm. cxix. 27.)

The quantity of creatinine in urine may be very exactly estimated by precipitation with an alcoholic solution of chloride of zinc. 300 cc. of urine are treated with milk of lime and chloride of calcium as above; the liquid, filtered after standing for two hours, is evaporated to dryness over the water-bath; the residue, while still warm, is digested for 4 or 5 hours with 30 or 40 cc. alcohol of  $95^{\circ}$ ; the liquid is filtered; the residue washed with small quantities of alcohol; the liquid, evaporated if necessary to a volume of 40 or 50 cc., is mixed, after cooling, with 0.5 cc. of an alcoholic solution of chloride of zinc (density 1.2), then briskly agitated, and left to itself for 3 or 4 days in a cellar; and the crystals thus obtained are washed on a weighed filter with a small quantity of alcohol, then dried at  $100^{\circ}$  C. and weighed. In this manner the quantity of creatinine voided in 24 hours in the urine of a healthy man weighing 54.5 kil. was found to be 1.166 grm., that is to say, 0.0214 grm. per kilogramme.

2. *From Horse-urine.*—The urine, which has an alkaline reaction, is neutralised with hydrochloric acid, evaporated to a small bulk, and then mixed with an additional quantity of hydrochloric acid; the liquid separated from the precipitated hippuric acid is neutralised with milk of lime, and evaporated nearly to dryness over the water-bath; the residue repeatedly boiled out with alcohol; and the alcoholic solution mixed with a small quantity of chloride of zinc: it then gradually deposits a brownish-yellow precipitate of zincchloride of creatinine, from which creatine and creatinine may be obtained as above. (Socoloff, Ann. Ch. Pharm. lxxviii. 243.)

3. *From Calves' urine.*—The fresh urine evaporated to a small bulk over the water-bath, and filtered while hot from the amorphous precipitate thereby formed, yields, after a few days, a crystalline mass consisting of allantoin, together with a large quantity of phosphate of sodium and ammonium; and on washing this crystalline

mass with cold water, and recrystallising the residue, crystals of pure allantoin are obtained. The mother-liquor filtered from the allantoin is mixed with alcohol, which throws down sulphates, mucous matter, the greater part of the phosphates, and a large quantity of colouring matter; and the filtrate, which is still considerably coloured, is freed from the remainder of the phosphoric acid by means of chloride of calcium, and lastly mixed with a concentrated solution of chloride of zinc; it then yields a precipitate of zincochloride of creatine, which continues to increase for several days. (Socoloff.)

4. *From Blood*.—A considerable quantity of fresh ox-blood (about 5 quarts) is freed from fibrin and blood-corpuscles by stirring, and from albumin by heat; then filtered through linen, and evaporated over the water-bath with addition of a little powdered gypsum, which removes an albuminous substance not coagulable by heat, as well as some additional blood-corpuscles, and precipitates the saponifiable fats. The liquid is then evaporated to one-fourth of its bulk, again filtered, and the colourless filtrate evaporated to dryness at a very gentle heat, whereupon nearly all the chloride of sodium crystallises out. On treating the residue with small quantities of absolute alcohol till nothing more is dissolved, and expelling the greater part of the alcohol by heat, the solution yields, on cooling, Boudet's *seroline* (Ann. Ch. Phys. lii. 337), the quantity of which increases on addition of a small quantity of water. The liquid filtered from the seroline yields, on addition of a small quantity of solution of chloride of zinc, sometimes immediately, sometimes after a few hours, a partly crystalline, partly amorphous precipitate, which is but partially soluble in boiling water. The insoluble portion is resinous, and appears to be a compound of chloride of zinc with a peculiar organic substance; the soluble portion consists of the zincochloride of creatinine. The quantity thus obtained is, however, but small. (Verdeil and Marcet, J. Pharm. [3] xx. 89.)

5. *From Muscular Flesh*.—The mother-liquor of creatine is treated with alcohol to precipitate the insolate of potassium or barium; the filtrate evaporated over the water-bath; the residue boiled out with alcohol, which takes up all the creatinine, together with a little creatine, and leaves a residue consisting chiefly of chloride and lactate of potassium; the filtrate mixed with chloride of zinc; and the crystals of zincochloride of creatinine, which form after a while, decomposed as above with hydrated oxide of lead. (Liebig.)

6. *From Creatine*.—*a*. Hydrochloric acid gas is passed to saturation over creatine heated to 100° in a Liebig's drying apparatus, then dry air as long as water continues to escape; or the solution of creatine in strong hydrochloric acid is evaporated to dryness in the water-bath. The hydrochlorate of creatinine obtained by either of these methods is then dissolved in 24 pts. of water; the solution kept at the boiling heat in a basin; perfectly pure hydrated oxide of lead macerated in water added to it by small portions till it becomes neutral or slightly alkaline, and then three times as much of the hydrated oxide of lead, until the liquid becomes pasty from formation of oxychloride of lead. The liquid is then filtered and the precipitate well washed; the filtrate treated with a small quantity of blood-charcoal to remove any lead that may still remain dissolved; the liquid again filtered, and the filtrate evaporated and cooled to the crystallising point (Liebig).—*b*. The solution of 1 pt. creatine in 1 pt. oil of vitriol and 3 pts. water is evaporated till all moisture is removed; the remaining sulphate of creatinine boiled with water and very pure carbonate of barium, till it becomes alkaline; and the solution filtered and left to crystallise. (Liebig.)

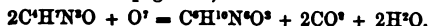
*Properties*.—Colourless prisms belonging to the monoclinic system. Dominant faces  $\infty P$ ,  $\infty P$ ,  $\infty P$ . Inclination of the faces  $\infty P$ :  $\infty P$  = 69° 24';  $\infty P$ :  $\infty P$  in the plane of the orthodiagonal and principal axis = 98° 20'. Creatinine in the state of concentrated solution has a caustic taste, like that of dilute ammonia. It blues reddened litmus, and reddens turmeric (Liebig). Dissolves in 11.5 pts. of water at 16° C., and much more abundantly in hot water; in 102 pts. of absolute alcohol at 16°, and more abundantly in hot alcohol, from which it crystallises on cooling. (Liebig.)

				Liebig.		
Calculation.				From Urine.	From Flesh.	From Creatine.
C <sup>4</sup>	.	48	42.48	42.64	41.70	42.54
H <sup>7</sup>	.	7	6.19	6.23	6.23	6.38
N <sup>3</sup>	.	42	37.17	37.41	.	37.20
O	.	16	14.16	13.72	.	13.88
C <sup>4</sup> H <sup>7</sup> N <sup>3</sup> O		113	100.00	100.00		100.00

*Decompositions*.—1. Creatinine, under certain circumstances, takes up 1 at. water, and is reconverted into creatine. The dilute solution of hydrochlorate or sulphate of creatinine slightly supersaturated with ammonia and evaporated, yields a few crystals of creatine (Heintz). Creatinine enclosed in a bottle with sufficient water to dissolve



it, yields in the course of six months a few crystals of creatine; if ammonia be added to the liquid, the quantity of creatine produced is considerably greater. The same transformation takes place in presence of neutral salts, and is accelerated by heat (Dessaigues, J. Pharm. [3] xxxii. 41; see also *Zincochloride of Creatinine, infra*). 2. Creatinine is decomposed by *mercuric oxide* in the same manner as creatine (p. 98), yielding methyluramine (Dessaigues); also by permanganate of potassium (Neubauer). 3. *Nitrous acid* passed into the aqueous solution of creatinine converts it, with evolution of carbonic acid, into the nitrate of a very weak base,  $C^4H^1N^3O^3$  (Dessaigues, *loc. cit.*; see also page 102):



4. Heated with *iodide of ethyl* and alcohol or ether, it yields iodide of ethyl-creatinine and hydriodate of creatinine.

*Sulphate of Creatinine.*  $C^4H^1N^3O$ .—An aqueous solution of creatinine saturated at a boiling heat and mixed with dilute sulphuric acid till it acquires a strong acid reaction, leaves on evaporation a white mass, whose solution in hot alcohol becomes turbid on cooling, then clear, and deposits transparent, colourless, quadratic tables, which remain transparent at  $100^\circ$ . (Liebig.)

*Hydriodate of Creatinine.*  $C^4H^1N^3O.HI$ , is produced, together with iodide of ethyl-creatinine, in the preparation of that compound (p. 102), and remains in the mother-liquor after the latter has crystallised out. It is very soluble in water and in alcohol, and may be obtained, by repeated crystallisation from water, in large transparent, somewhat yellowish crystals. The aqueous solution mixed with acetate of sodium and chloride of zinc, yields a precipitate of zinc-chloride of creatinine. (Neubauer.)

*Hydrochlorate of Creatinine.*  $C^4H^1N^3O.HCl$ . *Preparation* (ii. 100, 6).—Crystallises from solution in boiling alcohol in transparent colourless prisms, and, by evaporation of the aqueous solution, in transparent laminae which redden litmus. Dissolves very readily in water. (Liebig.)

*Zincochloride of Creatinine.*  $C^4H^1N^3O.ZnCl$ . *Preparation*.—1. (p. 100).—2. By mixing creatinine and chloride of zinc in the state of concentrated aqueous solutions. Both processes yield, with greater rapidity as the mixture is more concentrated, delicate needles united in nodules, or prisms (Pettenkofer), belonging to the monoclinic system, with terminal faces inclined  $82^\circ 30'$  to the principal axis (K. Schmidt, Ann. Ch. Pharm. lxi. 332). The crystals give off only a trace of hygroscopic water at  $120^\circ C$ . When the creatinine is separated from this compound by means of hydrated oxide of lead or sulphide of ammonium (p. 99), more than  $\frac{1}{2}$  of it is found to be converted into creatine, and in larger proportion, apparently, as the solution of the zinc-compound used was more dilute. If, therefore, after the creatine has been separated from the resulting liquid by evaporation and cooling, with addition of alcohol, the mother-liquor containing the rest of the creatinine be repeatedly precipitated with chloride of zinc, and the precipitate decomposed, &c., nearly all the creatinine may be converted into creatine (Heintz and Dessaigues). Zinc-chloride of creatinine dissolves sparingly in alcohol, but is insoluble in strong alcohol and in ether (Pettenkofer). It dissolves in 9217 pts. alcohol of  $98^\circ$ , and in 5743 pts. alcohol of  $87^\circ$ . (Neubauer.)

*Chloride of zinc* likewise combines with *hydrochlorate of creatinine*, forming the compound  $C^4H^1N^3O.HCl.ZnCl$ , which is obtained in large crystals, very soluble and strongly acid to the taste, by dissolving the zinc-chloride of creatinine in hydrochloric acid, and evaporating to a syrup (Dessaigues, J. Pharm. [3] xxxii. 43). The solution mixed with acetate of sodium, yields a precipitate of zinc-chloride of creatinine. (Neubauer, Ann. Ch. Pharm. xx. 267.)

Creatinine also forms with *chloride of cadmium*, a crystallised compound  $C^4H^1N^3O$ .  $CdCl$ , more soluble in water than the zinc-compound, and sometimes appearing to crystallise with 1 at. water. (Neubauer.)

With *cupric salts*, creatinine forms crystallisable double salts of a fine blue colour. (Liebig.)

When mixed in aqueous solution with *corrosive sublimate*, it immediately forms a white curdy precipitate, which changes in a few minutes to a mass of delicate colourless needles (Liebig). With *mercuric nitrate*, it forms a crystalline compound,  $2(C^4H^1N^3O.HgNO^3).Hg^2O$ , which, when decomposed by sulphydric acid, yields fine crystals of nitrate of creatinine. (Neubauer.)

With concentrated solution of *nitrate of silver*, it coagulates immediately into a mass of delicate white needles, which dissolve readily in hot water, and crystallise out again unchanged on cooling (Liebig). According to Neubauer, they contain  $2(C^4H^1N^3O.AgNO^3).Ag^2O$ .

The clear mixture of dilute hydrochlorate of creatinine and *dichloride of platinum* (or of hydrochloric acid, creatine, and dichloride of platinum), yields, by slow evapo-

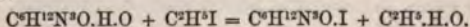
ration, transparent, aurora-red prisms, and by quicker evaporation, granules which dissolve readily in water, less quickly in alcohol, and contain 30.53 per cent. platinum, whence they probably consist of  $C^4H^7N^3O.HCl.PtCl^2$ . (Liebig.)

**Ethyl-creatinine.**  $C^4H^{12}N^3O = C^4H^7(C^2H^5)N^3O$  (Neubauer, Ann. Ch. Pharm. xix. 51; xx. 257).—The iodide of this base,  $C^4H^{12}N^3OI$ , is produced by enclosing 30 grms. of creatinine with rather more than an equivalent quantity of iodide of ethyl and about 40 per cent. of absolute alcohol, in a sealed tube and heating the mixture to  $100^\circ C$ . for several hours. A crystalline pulp is thus obtained, which, when purified by several recrystallisations from absolute alcohol, yields the iodide in long shining needles, very soluble both in water and in alcohol.

By treating the iodide with oxide of silver, carefully avoiding an excess, and evaporating the filtrate in vacuo, a radio-crystalline mass is obtained, consisting of the hydrate of ethyl-creatinine  $\left. \begin{matrix} C^4H^{12}N^3O \\ H \end{matrix} \right\} O + \frac{1}{2} aq.$  very soluble in water and alcohol, insoluble in ether. From solution in warm absolute alcohol it crystallises on cooling, in fine needles, grouped in nodules. It is not deliquescent. The aqueous solution is strongly alkaline, has a bitter taste, precipitates sesquichloride of iron and salts of aluminium, and expels ammonia from its salts when heated with them.

The chloride  $C^4H^{12}N^3OCl$  is obtained by slightly supersaturating the aqueous solution of the base with hydrochloric acid, and evaporating, as a crystalline mass composed of interlaced needles, very soluble in water and alcohol, insoluble in ether. The solution, mixed with dichloride of platinum, yields the chloroplatinate,  $C^4H^{12}N^3OCl.PtCl^2$ , in fine prisms.

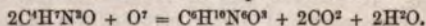
Hydrate of ethyl-creatinine, heated in a sealed tube with iodide of ethyl, does not yield a compound containing another atom of ethyl, but merely iodide of ethyl-creatinine and alcohol:



Hence ethyl-creatinine may be regarded as an ammonium-base, and creatinine itself as a tertiary amine,  $N.(C^4H^7N^3O)^{tr}$ .

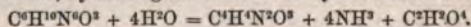
*Bases produced from Creatine and Creatinine by the action of Nitrous Acid.*

**a.**  $C^4H^{10}N^3O^2$ . (Dessaigues, Compt. rend. xli. 1258; Ann. Ch. Pharm. xlvii. 339.)—When nitrous acid gas is passed into an aqueous solution of creatinine, carbonic acid escapes, the liquid becomes brown and turbid, and after a few hours the nitrate of the base,  $C^4H^{10}N^3O^3$ , separates in small yellowish indistinct crystals, which become thick if left for some time under the liquid. The reaction is:



This compound, which appears to be likewise formed in small quantity by the action of nitrous acid on creatine, is a very weak base, its salts being partially decomposed even by solution in water. Ammonia added to the solutions throws down the base as a white, amorphous, tasteless powder, insoluble in water, but soluble in dilute acids at a gentle heat. Some of the salts crystallise from their solutions on cooling. The hydrochlorate,  $2C^4H^{10}N^3O^3.3HCl + 6H^2O$ , forms long deeply striated prisms; the chloroplatinate, which is moderately soluble in water, forms large crystals, consisting of  $2C^4H^{10}N^3O^3.3HCl.3PtCl^2 + 6H^2O$ .

**β.**  $C^4H^8N^3O^3$ . (Dessaigues, loc. cit.)—Produced, together with oxalic acid and chloride of ammonium, by heating the base **a** with hydrochloric acid:



Crystallises in long shining prisms or laminae; dissolves slowly in cold water, easily in hot water, slightly in ether; has an unpleasant, almost metallic taste; melts and volatilises without decomposition, and burns with flame without leaving any residue. It has a slight acid reaction; does not precipitate the salts of calcium, barium, lead, copper, or zinc, or chloride of mercury, or nitrate of silver in dilute solution. Dessaigues regards this body as identical with that which Liebig observed to be produced, together with sarcosine, by the action of baryta on creatine at the boiling heat (p. 97). Städeler (Ann. Ch. Pharm. cxviii. 151) points out that it has the composition of methyl-para-

banic acid,  $C^3H(CH^3)N^2O^3 = N^2.(CO)^2(C^2O^2).CH^3.H$ .

**γ.**  $C^4H^8N^3$ . (Dessaigues, Compt. rend. xxxviii. 839.)—When nitrous acid is passed into a solution of creatine in nitric acid, a large quantity of gas is evolved, and on neutralising with potash, separating the greater part of the nitrate of potassium by crystallisation, and adding nitrate of silver, crystals are obtained, consisting of  $C^4H^8N^3.AgNO^3$ . They dissolve in hot water, and after several crystallisations assume the form of long white needles. When decomposed by excess of hydrochloric acid,



they yield the nitrate,  $C^3H^3N.HNO^3$ , in the form of a fibrous mass of small prisms having a very sour taste. The chloromercurate crystallises in long prisms.

**CREDNERITE.** *Cupriferosus Manganese.*  $3Cu^2O.2Mn^4O^3$ —A mineral found near Friedrichsrode in the Thüringer Wald, together with psilomelane and hausmannite. It occurs in crystallo-laminar aggregations, cleaving with moderate distinctness in two directions parallel to the sides of a monoclinic prism, very distinctly parallel to the base. Fracture uneven. Colour iron-black. Streak black. Lustre vitreous, strongest on the perfect cleavage-face. Opaque. Specific gravity = 4.9 to 5.1. Hardness = 4.0—4.5. Thin laminae melt, at the edges only, when strongly heated before the blowpipe. With borax it forms a dark violet glass; with phosphorus-salt a green glass, becoming blue on cooling, and copper-red in the inner flame. Hydrochloric acid dissolves it, with evolution of chlorine, forming a green solution.

Analyses *a, b, c*, by Rammelsberg (Pogg. Ann. lxxxiv. 559); *d* by Credner (*ibid.* lxxiv. 555).

	Mn <sup>2</sup> O	O	Cu <sup>2</sup> O	Ba <sup>2</sup> O	Ca <sup>2</sup> O	H <sup>2</sup> O	Gangue.	
<i>a.</i>	64.24	8.83	23.73	2.01	—	—	—	= 98.81
<i>b.</i>	56.29	8.58	32.35	3.08	0.76	—	—	= 101.06
<i>c.</i>	52.55	5.78	40.65	1.48	—	—	—	= 100.46
<i>d.</i>	51.06	—	42.73	0.52	0.63	0.25	0.63	= 95.82

The formula  $3Cu^2O.2Mn^4O^3$  requires 42.9 per cent.  $Cu^2O$ , and 57.1  $Mn^2O$ ; the mineral often contains excess of oxide of manganese.

**CRENIC and APOCRENIC ACIDS.** (Berzelius, Pogg. Ann. xiii. 84; Mulder, Ann. Ch. Pharm. xxxvi. 243).—Organic acids existing, according to Berzelius, in vegetable mould and in the ochreous deposits of ferruginous waters. (The word *crenic* is derived from *κρήνη*, a spring.) They were first obtained from the mineral water of Porla in Sweden. According to Berzelius, the yellow deposit which forms in ferruginous waters contains these acids in the form of basic salts. They are extracted by boiling the deposit with potash, filtering, supersaturating the liquid with acetic acid, and adding a solution of acetate of copper, as long as a dark brown precipitate continues to form. This precipitate contains the apocrenic acid. The liquid is filtered, saturated, or slightly supersaturated with carbonate of ammonium, and acetate of copper again added as long as a greenish-white precipitate is produced. The precipitation is completed by heating the mixture which contains the crenic acid to 80° C.; the crenic acid is more abundant than the apocrenic. Both precipitates are decomposed by suspending them in water, and passing a stream of sulphuretted hydrogen through the liquid.

The *crenic* acid is isolated by evaporating the filtered liquid in vacuo. The product thus obtained still retains a certain quantity of earthy crenates, from which it may be separated by means of absolute alcohol, which dissolves the acid and leaves the salts, and evaporating the alcohol in vacuo. As thus obtained, it is pale yellow, uncrystallisable, transparent, hard, and fissured; its taste is acid at first, afterwards astringent. With the alkalis it forms neutral and acid salts, which are uncrystallisable, soluble in water, insoluble in alcohol, and resemble vegetable extracts in appearance. They are yellow, and turn brown in the air from formation of apocrenic acid.

*Apocrenic acid* is brown, sparingly soluble in water, more soluble in absolute alcohol, and has a very astringent taste. The apocrenates of the alkalis resemble the crenates, excepting that they are black.

Both acids displace acetic acid by evaporation. Apocrenic acid dissolves immediately in alkaline acetates. The ferrous salts of both acids are soluble in water, but their ferric salts are insoluble.

According to Berzelius, both crenic and apocrenic acid contain nitrogen and give off ammonia by dry distillation. Mulder supposes that the nitrogen found in them is in the form of an ammonium-salt, and may be completely removed by acetic acid. Mulder represents crenic acid by the formula  $C^{12}H^{12}O^8$ , and apocrenic acid by  $C^{12}H^{12}O^{12}$ ; but these acids have not yet been obtained in a sufficiently definite state to enable us to fix their formulæ.

**CREOSOL.** The principal constituent of wood-creosote (p. 104).

**CREOSOTE.** (Reichenbach [1832], Schw. J. lxvi. 301, 345; lxvii. 1, 57; lxviii. 352. Ettling, Ann. Ch. Pharm. vi. 209. Laurent, Compt. rend. xi. 124; xix. 574. Deville, Ann. Ch. Phys. [3] xii. 228. Goup-Besanez, Ann. Ch. Pharm. lxxviii. 231; lxxxvi. 223. Völkcl, *ibid.* lxxxvi. 93; lxxxvii. 306. Hlasiwetz, *ibid.* cvi. 339. On the Preparation of Creosote: E. Simon, Pogg. Ann. xxxii. 129. Hübschmann, Ann. Ch. Pharm. xi. 40. Köne, *ibid.* xvi. 63. Krüger, Buchner's Repert. Pharm. xviii. 273. Buchner, *ibid.* xlix. 84. Cozzi, *ibid.* lv. 693.)—The substance known in commerce by the name of *creosote* is often

merely hydrate of phenyl more or less impure; but the true creosote extracted by Reichenbach from wood-tar is a perfectly distinct body, and does not exhibit all the characters of hydrate of phenyl. It is to the true creosote that wood-vinegar, tar-water, soot, and wood-smoke owe their power of arresting the putrefaction of meat and other animal substances. The name *creosote* is derived from *κρέας*, flesh, and *σώζω*, to save.

**Preparation.**—When wood-tar is distilled till the residue acquires the consistence of a pitchy mass, the liquid collected in the receiver is formed of several distinct layers, the lowest of which contains the creosote. On saturating it with carbonate of sodium and leaving it at rest, a yellowish oil rises to the surface. This oil is decanted, and rectified in a glass retort, the lighter portion of the distillate being rejected and the heavier portion collected and ignited with potash-solution of specific gravity 1.12. The creosote then dissolves in the alkaline liquid, while the hydrocarbons with which it is mixed remain undissolved. The alkaline solution is decanted and boiled for some time in contact with the air, to resinise a foreign substance dissolved in the potash, after which the liquid is filtered and the creosote set free by addition of sulphuric acid. The creosote thus obtained is not yet pure; it requires to be again distilled several times with alkaline water, then dissolved in potash, to free the creosote from insoluble hydrocarbons, and separated from the alkaline solution by sulphuric acid. These operations must be repeated till the creosote dissolves in potash without residue, after which the creosote is to be finally distilled at  $200^{\circ}\text{C}$ ., and dried over chloride of calcium.

**Properties.**—Creosote is a colourless, oily, strongly refracting liquid, having a disagreeable penetrating odour like that of smoked meat, and a burning taste. Specific gravity 1.037 at  $20^{\circ}\text{C}$ . (Reichenbach), 1.040 at  $11.5^{\circ}$  (Gorup-Besanez), 1.076 at  $15.5^{\circ}$  (Vöckel). It does not solidify at  $-27^{\circ}\text{C}$ . Boils at  $203^{\circ}$  (Reichenbach); between  $203.5^{\circ}$  and  $208^{\circ}$  (Gorup-Besanez), and distils in great part without alteration. When pure it does not become coloured by exposure to the air. It burns with a smoky flame. Does not conduct electricity.

Creosote is sparingly soluble in water, but mixes in all proportions with alcohol, ether, bisulphide of carbon, naphtha, and acetic ether. It dissolves sulphur, phosphorus, selenium, oxalic, citric, tartaric, benzoic and stearic acids, resins, and several colouring matters. With the aid of heat it dissolves several metallic salts, *e. g.* the chlorides of calcium and tin, the acetates of potassium, sodium, ammonium, zinc, &c., and deposits them in the crystalline state on cooling.

It imparts a blue colour to *ferrie salts*, and reduces nitrate of *silver*, and the salts of *mercury, gold, and platinum*. When dropped on recently prepared oxide of silver it produces a kind of explosion, the silver being partly reduced, and oxalate of silver formed, together with several resinous compounds.

The composition of creosote is not yet definitely fixed. The following are the analyses which have been made of it:

	Etling.		Gorup-Besanez.			
C . . .	75.72	74.53	75.32	75.72	74.78	74.68
H . . .	7.80	7.87	7.84	7.94	7.98	7.84
O . . .	16.48	17.60	16.84	16.34	17.24	17.48
	100.00	100.00	100.00	100.00	100.00	100.00

	Dewille.			Vöckel.		
C . . .	72.30	72.54	72.92	72.48	72.53	72.35
H . . .	7.60	7.60	8.16	7.04	7.10	7.16
O . . .	20.10	19.86	18.92	20.48	20.37	20.49
	100.00	100.00	100.00	100.00	100.00	100.00

Gorup-Besanez deduces from his analyses the formula  $\text{C}^{13}\text{H}^{16}\text{O}^2$  (calc. 76.47 C; 7.84 H). Vöckel gives the formula  $\text{C}^{12}\text{H}^{14}\text{O}^2$  (72.72 C; 7.07 H); neither of these formulae agrees well with the analyses. According to Hlasiwetz, creosote is a compound ether derived from an acid,  $\text{C}^8\text{H}^{10}\text{O}^2$ , which, when treated with bases, forms salts having the composition  $\text{C}^8\text{H}^8\text{MO}^2$ , and yielding the acid itself when distilled with dilute sulphuric acid (see p. 105).

**Decompositions.**—Creosote is decomposed by *chlorine*, with evolution of hydrochloric acid and formation of a chlorinated compound, which is decomposed by distillation. *Bromine* is absorbed in large quantity by creosote, yielding, according to Dewille, a crystalline acid, having the composition of creosote in which half the hydrogen is replaced by bromine. *Iodine* dissolves in creosote, forming a brown liquid.

When creosote is acted upon at a gentle heat by a mixture of *hydrochloric acid* and *chlorate of potassium*, the action being continued for several days, and arrested as



soon as an abundant evolution of chlorine takes place, a crystalline mass is obtained from which cold alcohol extracts a substance crystallising in large rhomboidal tables, leaving another compound in the form of yellow scales. (Gorup-Besanez).

The rhomboidal tables give by analysis 39.8 per cent. C, and 1.9 H, which Gorup represents by the formula  $C^{12}H^1Cl^3O^2$ , designating the compound as *pentachloroxylin*. Gerhardt, however (*Traité*, iii. 24), prefers the formula  $C^8H^2Cl^4O^2$  (calc. 40 per cent. carbon, and 2 hydrogen); according to which it is homologous with trichloroquinone. The yellow scales give by analysis (mean) 36.7 C, 1.5 H, and 50.6 Cl, which Gorup represents by the formula  $C^{12}H^1Cl^6O^2$  (*hexachloroxylin*), while Gerhardt gives the formula  $C^8H^2Cl^4O^2$ , homologous with tetrachloroquinone. When the yellow scales are suspended in water and sulphurous acid gas passed through the liquid, the scales are converted into brownish-white four-sided prisms, which dissolve in a mixture of alcohol and ether, yielding a yellow solution, which, by spontaneous evaporation, deposits long violet needles and reddish prisms, the latter containing about the same quantity of carbon as the yellow scales, but more hydrogen (2.23 to 2.39 per cent.). Hence these products would appear to be related to the yellow scales in the same manner as the chlorinated hydroquinones are to the chlorinated quinones. All these compounds require further investigation, but their formation is sufficient to show that creosote from wood-tar is a very different thing from hydrate of phenyl, the so-called *coal-tar creosote*.

Creosote partakes of the nature of an acid; it dissolves in caustic alkalis, and is decomposed by potassium, with elimination of hydrogen. Two potassium-salts have been formed, also sodium, ammonium, barium, lead, ethyl, and benzoyl-salts.

**Potassium-salts.**—*a. Neutral*,  $C^8H^2KO^2.2H^2O$ . Obtained by heating creosote with solid hydrate of potassium to about  $130^{\circ}C$ . in an atmosphere of hydrogen, and crystallising the product from ether. It is then obtained in thin soft prisms or scales, of dazzling whiteness and satiny lustre. It dissolves readily also in water and alcohol, crystallising from the aqueous solution in soft interlaced needles. When thoroughly freed from mother-liquor by pressure and dried, it may be preserved without alteration; otherwise it quickly turns bluish-green, and ultimately brown on exposure to the air. The same is the case with all the creosote-salts; hence the necessity of excluding the air during their preparation.—*b. Acid salt*,  $C^8H^2KO^2.C^8H^4O^2$ . Obtained by treating creosote with potassium in an atmosphere of hydrogen, and crystallising from ether. Resembles the neutral salt in appearance and in most of its properties, but is decomposed by water. (Hlasiwetz.)

**Sodium-salts.**—Creosote behaves with sodium and hydrate of sodium much in the same manner as with potassium and its hydrate; but the sodium-salts have not yet been obtained in definite form. (Hlasiwetz.)

**Barium-salt,  $2C^8H^2BaO^2 + 3H^2O$ .—Prepared like the neutral potassium-salt. Forms dazzling white scales, having a satiny lustre, quite inodorous, and permanent when pure. Gives off its water at  $100^{\circ}C$ . (Hlasiwetz.)**

**Lead-salt,  $4C^8H^2PbO^2.Pb^2O + 2H^2O$ .—The neutral potassium-salt mixed with acetate of lead yields a bulky white precipitate, which, when dried in vacuo, exhibits this composition. (Hlasiwetz.)**

**Ethyl-compound,  $C^8H^4(C^2H^5)O^2$ .—Obtained by heating the neutral potassium-salt with iodide of ethyl in a sealed tube, distilling, removing the last traces of iodine by agitation with silver, and rectifying. Oily liquid, having a slight yellowish tinge and faint aromatic odour.**

**A benzoyl-compound,  $C^8H^4(C^7H^5O)O^2$ , appears to be formed by treating the neutral potassium-salt with chloride of benzoyl. (Hlasiwetz.)**

**Creosol**,  $C^8H^4O^2$ .—By decomposing the neutral potassium-salt of creosote with dilute sulphuric acid, washing with water, rectifying, and collecting the portion which distils over at  $219^{\circ}C$ . (which is by far the larger portion, small quantities only distilling at lower and at higher temperatures), a colourless oil is obtained, agreeing in composition with the formula  $C^8H^4O^2$  (69.6 C, and 7.2 H). It is of the consistence of creosote, refracts light strongly, has an aromatic odour like that of vanilla, and burning taste; anhydrous; but little altered by keeping. Specific gravity 1.0894 at  $13^{\circ}C$ . Vapour-density 4.98 (by calculation to 2 vols. 4.79). It is not more soluble in water than creosote; mixes in all proportions with alcohol, ether, glacial acetic acid, and alkaline leys. In a freezing mixture, it becomes viscid, but not solid. It reduces nitrate of silver, producing a specular deposit of the metal. Does not unite with the acid sulphites of the alkali-metals, but forms with ammonia, either in the state of gas or in strong aqueous solution, a crystalline salt, sparingly soluble in water, and having the composition  $C^8H^4(NH^4)O^2.C^8H^{10}O^2$ , analogous to the acid potassium-salt above described. With potash and baryta it behaves like creosote, yielding the salts  $C^8H^4KO^2$  and  $C^8H^4BaO^2$ ; the preparation of which is moreover much easier with this oil than with creosote. Bromine acts violently on it, forming a crystalline com-



pound, containing  $C^6H^3Br^3O^4$ . The same compound is formed by the action of bromine on crude creosote; it does not however solidify at once, but forms a crystalline pulp, from which the pure compound may be obtained by dissolving the pulp in a small quantity of acetic acid, leaving the solution over night, and pressing the deposited crystals to free them from mother-liquor. It is formed by the replacement of 5 at. hydrogen by bromine in a double molecule of creosol.

*Trichlorocresol*,  $C^6H^3Cl^3O^2$ , is formed by introducing creosol into a large flask filled with chlorine. The whole solidifies in about 24 hours, and the product may be purified by crystallisation from acetic acid. (Hlasiwetz.)

It appears then that creosote consists mainly of an oil capable of forming salts with bases, and having the composition  $C^8H^{10}O^2$ . This oil (cresol) is likewise contained in the product of the destructive distillation of guajac resin—this product consisting, according to Hlasiwetz, of *guajacol*,  $C^8H^8O^2$ , and the homologous compound, *creosote-guajacol* or *creosol*,  $C^8H^{10}O^2$ . Creosote itself is probably a compound of the form  $C^8H^x(R)O^2$  or  $C^8H^x(R)O^4$ , in which R denotes a radicle free from oxygen. (Hlasiwetz, *loc. cit.*)

**CRESOTIC ACID.**  $C^8H^8O^2 = \begin{matrix} C^8H^7O^2 \\ H \end{matrix} \} O$ . (Kolbe and Lautemann, Ann. Ch.

Pharm. cxv. 203.)—An acid isomeric with carbocresylic acid, produced by the action of sodium and carbonic anhydride on cresylic alcohol ( $C^8H^8O + CO^2 = C^8H^8O^2$ ). The resulting mixture of carbocresylate and cresotate of sodium is treated with hydrochloric acid, whereby the carbocresylic acid is resolved into carbonic anhydride and cresylic alcohol, while the cresotic acid remains undecomposed, and may be washed out by means of a strong solution of carbonate of ammonia, the liquid on evaporation yielding the pure acid in fine large prisms. The acid dissolves sparingly in water, easily in alcohol and ether. It melts at  $153^\circ C$ . and solidifies at  $144^\circ$ . By mixing it with salicylic acid (which melts at  $169^\circ$ ), a mixture of lower melting point is obtained: a mixture of 1 pt. cresotic acid and 4 pts. salicylic acid was found to melt at  $139^\circ$ .

Cresotic acid produces a deep violet colour with sesquichloride of iron. When heated with *caustic baryta*, it is resolved into carbonic anhydride and cresylic alcohol.

**CRESOXACETIC ACID.**  $C^8H^{10}O^3$ ?—An acid produced by the action of monochloroacetic acid on cresylate of sodium. Its copper salt,  $C^8H^7CuO^3 + aq.$ , is green, and sparingly soluble. (Heintz, Berl. Akad. Ber. 1860, p. 464.)

**CRESS, OIL OF.** The herb of *Lepidium ruderale* and the inodorous seed of *Lepidium ruderale*, *L. sativum*, and *L. campestre*, bruised and macerated in water, yield by distillation a milky water, from which, by repeated fractional rectification in glass vessels (copper would exert a decomposing action), a yellow oil may be obtained. This oil, after further rectification, is colourless, but turns yellow again on exposure to light. It is heavier than water, neutral, exhibits the refreshing but somewhat alliaceous odour and biting taste of water-cresses, and, when its vapour is inhaled in rather large quantity, produces dryness in the throat and headache. It cannot be distilled undecomposed without water. By oxidation with nitric acid, it yields sulphuric acid. With mercurous nitrate it forms a black precipitate of sulphide of mercury; with corrosive sublimate a white precipitate; with nitrate of silver, sometimes white, sometimes black; with dichloride of platinum in alcoholic solution, an orange-yellow precipitate after a while. Aqueous potash and ammonia have no action on this oil. It dissolves with red colour in oil of vitriol, and may be separated again by water. It dissolves slowly in water, readily in alcohol and ether. (Pless, Ann. Ch. Pharm. lviii. 36.)

The fresh leaves of *Lepidium latifolium* yield by distillation with water, a neutral oil heavier than water, together with a milky, strong-smelling and sharp-tasting water, which loses its sharpness by exposure to the air, and likewise in a few hours after being mixed with chlorine (whereupon it precipitates chloride of barium); it gradually forms a black precipitate with nitrate of silver; blackens metallic silver after a while; and is deprived of its taste and odour by charcoal powder. (Stendel, Diss. de acredine nonnull. vegetab. Tübingen, 1805.)

**CRESYLIC ALCOHOL.** *Hydrate of Cresyl.*  $C^8H^8O = C^8H^7.H.O$ .—This alcohol, homologous with hydrate of phenyl, was discovered in 1854 by Williamson and Fairlie (Chem. Soc. Qu. J. vii. 232), and further investigated by Duclos (Ann. Ch. Pharm. cix. 135). It occurs in variable quantity in the so-called coal-tar creosote, and is obtained by subjecting the portion of that liquid which boils between  $200^\circ$  and  $220^\circ C$ . to fractional distillation (Fairlie). It likewise exists, together with hydrate of phenyl and other compounds, in the tar of fir-wood, and is obtained therefrom by treating the oil which passes over in fractional distillation between  $150^\circ$  and  $220^\circ$ , with weak soda-ley, to separate hydrocarbons, supersaturating the alkaline liquid with sulphuric acid, and repeating the treatment with soda-ley and sulphuric acid, till the oil becomes perfectly



soluble in the alkaline liquid. The oil thus obtained is a mixture of phenylic and cresylic alcohols, which are separated by fractional distillation, the former boiling at 187° C.

Cresylic alcohol is a colourless, strongly-refracting liquid, which boils at 203° C. in the air (the same as wood-tar creosote, p. 104), and at 200° in an atmosphere of hydrogen. Analysis gave 77.4 to 77.7 per cent. carbon, and 8.05 to 2.20 hydrogen (calculation, 77.8 C. and 7.11 H). It is isomeric with benzylic alcohol (i. 578).

Cresylic alcohol is slightly soluble in water, and mixes in all proportions with alcohol and ether. According to Fairlie, it is quite insoluble in ammonia; but according to Duclos, it dissolves in ammonia as easily as phenylic alcohol.

Cresylic alcohol is decomposed by repeated distillation, a portion being apparently converted by the oxidising action of the air into hydrate of phenyl,  $C^6H^5O$ ; but in an atmosphere of hydrogen it may be distilled any number of times without alteration. Strong nitric acid at ordinary temperatures attacks it with explosive violence; but when treated with well-cooled nitric acid, it yields a red solution containing trinitrocresylic acid,  $C^6H^3(NO_2)_3O$ , homologous with picric acid. With dilute nitric acid it forms only a brown tarry mass (Fairlie); according to Duclos, the product is mononitrocresylic acid. With strong sulphuric acid, cresylic alcohol becomes rose-coloured, and forms sulphocresylic acid,  $C^6H^4O.SO_3$ . With pentachloride of phosphorus, cresylic alcohol yields chloride of cresyl,  $C^6H^4Cl$  (boiling at 197°C.), and phosphate of cresyl, which latter is converted by acetate of potassium into acetate of cresyl, and when distilled with ethylate of potassium, yields cresylate of ethyl  $C^6H^4.C^2H_5O$ , and phosphate of potassium. Mixed with an equal bulk of strong potash-ley, it forms, in the course of 24 hours, a few small crystals, apparently consisting of cresylate of potassium,  $C^6H^4KO$  (Fairlie). In contact with chloride of calcium or chloride of zinc, it appears to be converted into phenylic alcohol (Gladstone, *Chemical News*, ii. 98.)

Cresylic alcohol, treated with potassium or sodium, gives off hydrogen and forms a brownish mass, which, on cooling, solidifies to a mass of slender needles of cresylate of potassium or sodium, difficult to purify by crystallisation from ether (Duclos). Cresylate of sodium treated with monochloroacetic acid yields cresoxacetic acid. (Heintz, p. 207.)

#### Derivatives of Cresylic Alcohol.

**Nitrocresylic Acid**,  $C^6H^4NO_2 = \frac{C^6H^4(NO_2)}{H} \left. \vphantom{\frac{C^6H^4(NO_2)}{H}} \right\} O$ .—When very dilute nitric acid is gradually added to an aqueous solution of cresylic alcohol heated to 60° or 70° C., the liquid acquires an aromatic odour and yellowish-brown colour, without giving off red vapours, and ultimately deposits nitrocresylic acid in oily drops, which sink to the bottom of the vessel; they are washed with water and dried in vacuo.

Nitrocresylic acid is a yellowish-brown syrupy liquid, inodorous, bitter, easily soluble in alcohol, colours the skin yellow. It appears to unite with alkalis. (Duclos, *loc. cit.*)

**Dinitrocresylic Acid**,  $C^6H^3NO_2O = \frac{C^6H^3(NO_2)_2}{H} \left. \vphantom{\frac{C^6H^3(NO_2)_2}{H}} \right\} O$ .—This acid is prepared, not directly from cresylic alcohol, but by the action of nitric acid on sulphocresylic acid. A solution of 1 vol. sulphocresylic acid in 5 or 6 vols. water, or an equally dilute solution of cresylic alcohol in a small quantity of sulphuric acid, is heated with a small quantity of nitric acid diluted with its own bulk of water; the liquid is filtered from a resinous body which separates on cooling; and the filtrate is heated to boiling with addition of nitric acid. Dinitrocresylic acid then separates as a yellow oil, which dissolves in alcohol, but does not crystallise by evaporation. When slowly heated, part of it appears to sublime undecomposed; when quickly heated it detonates. (Duclos.)

Dinitrocresylate of Ammonium is easily soluble, but difficult to crystallise. (Duclos.)

**Trinitrocresylic Acid**,  $C^6H^2NO_3 = \frac{C^6H^2(NO_2)_3}{H} \left. \vphantom{\frac{C^6H^2(NO_2)_3}{H}} \right\} O$ .—Discovered by Fairlie, more fully investigated by Duclos. Homologous with trinitrophenic or picric acid. It is obtained—1. By adding fuming nitric acid in small portions to coal-tar creosote containing cresylic alcohol, in a vessel surrounded with ice. The liquid then assumes a deep red colour, and after the addition of a volume of nitric acid equal to that of the creosote, separates into two layers, the upper deep red, the lower black and tarry; the upper contains the trinitrocresylic acid (Fairlie).—2. By heating a dilute solution of sulphocresylic acid with nitric acid, filtering from the resinous body which separates, again heating the filtrate with nitric acid, and evaporating. The dinitrocresylic acid which first separates, is then converted, by the continued action of the nitric acid, into trinitrocresylic acid, which is found, together with oxalic acid, in the crystalline residue obtained on cooling. The oxalic acid is removed by washing, and

the trinitrocresylic acid may be obtained in the crystalline form by solution in alcohol and evaporation in vacuo. (Duclos.)

Trinitrocresylic acid crystallises in yellow needles, soluble in 449 pts. of water at 20° C, and in 123 pts. at 100° (less soluble therefore than picric acid). The solution has a fine yellow colour, reddens litmus, and imparts a yellow stain to wool and silk. It dissolves alcohol, ether, and benzene. It is separated from its aqueous solution by most mineral acids, but dissolves in excess of nitric acid more easily than in water. When heated a little above 100° C, it melts to a reddish-yellow oil, which solidifies in the crystalline form on cooling. At a higher temperature it deflagrates like picric acid. (Duclos.)

With solution of chloride of lime, or with hydrochloric acid and chlorate of potassium, it emits the odour of chloropicrin. (Duclos.)

*Trinitrocresylate of Ammonium*,  $\text{C}^7\text{H}^4(\text{NO}^2)^3\text{O}$ , crystallises in yellow needles easily soluble in water, less easily in alcohol; they deflagrate when heated. (Duclos.)

*Trinitrocresylate of Lead*,  $2\text{C}^7\text{H}^4\text{Pb}(\text{NO}^2)^3\text{O} \cdot \text{Pb}^2\text{O}$ .—When a boiling dilute solution of acetate of lead is mixed with trinitrocresylate of ammonium, this salt separates from the filtrate on cooling in microscopic needles which are moderately soluble in water, and detonate when heated. (Duclos.)

*Trinitrocresylate of Potassium*,  $\text{C}^7\text{H}^4\text{K}(\text{NO}^2)^3\text{O}$ , crystallises in small orange-red needles which are moderately soluble in water (Duclos); sparingly soluble in cold, easily in hot water (Fairlie), and detonate strongly when heated. (Duclos.)

**Sulphocresylic or Cresylsulphuric Acid**,  $\text{C}^7\text{H}^4\text{O}^3\text{SO}^3$ .—First obtained by Fairlie; further examined by Duclos. Not known in the free state. Cresylic alcohol is mixed with strong sulphuric acid, the liquid left to stand for about 24 hours at about 60° C., and then mixed with water, which does not separate any oil-drops. This liquid, saturated with carbonate of lead or carbonate of barium, and carefully evaporated, at last in vacuo, yields the corresponding sulphocresylates.

The *barium-salt*,  $\text{C}^7\text{H}^4\text{BaO}^3\text{SO}^3$ , is colourless, amorphous, and easily decomposable. The *lead-salt*,  $\text{C}^7\text{H}^4\text{PbO}^3\text{SO}^3$ , gradually dries up to an amorphous, colourless mass, which decomposes at 140° C.

**CRICHTONITE.** A variety of titaniferous iron, found at St. Christophe, near Orsans, in the Département d'Isère (Dauphiné), and regarded as a subspecies of ilmenite (*q. v.*)

**CRISPITE.** Syn. with RUTILE.

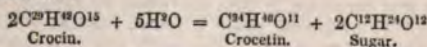
**CRITHMUM MARITIMUM.** *Sea-fennel.* An umbelliferous plant, growing on the sea-shore, containing volatile oil and free acetic acid. (Lavini, Geiger's Magaz. iv. 118.)

**CROCETIN.** See CROCIN.

**CROCIN.**  $\text{C}^{29}\text{H}^{42}\text{O}^{15}$ , or  $\text{C}^{30}\text{H}^{42}\text{O}^{30}$ .—The colouring matter of Chinese yellow berries, the fruit of *Gardenia grandiflora*. Discovered and partly examined by Mayer in 1858, more particularly by Rochleder (J. pr. Chem. lvi. 68), who regards it as identical with a substance which Quadrat obtained in an impure state from saffron, and to which he assigned the formula  $\text{C}^{29}\text{H}^{42}\text{O}^{11}$ .

To prepare crocin, the crushed yellow berries are boiled with alcohol; the expressed liquid is filtered, and the alcohol evaporated; the remaining aqueous solution, which deposits a liquid fatty acid and a crystalline substance, is filtered, diluted with water, and mixed with a large quantity of hydrate of alumina; the liquid, filtered after standing for several days, is precipitated with basic acetate of lead; the reddish-yellow precipitate is quickly collected on a filter, washed, suspended in water, and decomposed with sulphydric acid, the colouring matter then separating, together with the sulphide of lead; the precipitate, after washing with water, is well boiled with alcohol; and the filtrate is left to dry up in vacuo over sulphuric acid. The residue is then dissolved in a small quantity of water, filtered from a small quantity of separated sulphur, and again evaporated.

Crocin thus prepared yields, by trituration, a bright red powder, easily soluble in water and in alcohol, the solutions having the colour of dissolved chromic acid, and forming an orange-coloured precipitate with lead-salts. The concentrated aqueous solution mixed with strong sulphuric acid assumes first an indigo-blue, then a violet colour. The dilute aqueous solution boiled with dilute sulphuric or hydrochloric acid, is resolved into crocetin, which separates on cooling if the solution is not too dilute, and a colourless uncrystallisable sugar (amounting to 28.2 per cent. of the crocin), which remains in solution:





*Crocein*,  $C^{11}H^{16}O^{11}$ , or  $C^{11}H^{18}O^{11}$ .—To obtain this substance pure, the crocin should be boiled with the acid in an atmosphere of hydrogen or carbonic acid, as both crocin and crocein easily absorb oxygen.

Crocein is a dark red amorphous powder, slightly soluble in water, easily in alcohol. It turns blue in *sulphuric acid*, like crocin. Its solution forms a yellow precipitate with *lead-salts*. Stuffs mordanted with tin-salt acquire, by boiling in a solution of crocein, a dingy greenish yellow colour, which by treatment with ammoniacal water is converted into a brilliant yellow colour, unaltered by light and air. The yellow robes of the Chinese mandarins are dyed with the fruit of the *Gardenia*. (Handw. d. Chem. ii. 2<sup>e</sup> Aufl. ii. [3] 226.)

**CROCIDOLITE** (from *κροκίς*, wool). A silicate occurring in asbestos-like fibres, also massive, in the Griqua country, beyond the Orange river, South Africa, and in the micaceous porphyry of Wakenbach in the Vosges. Specific gravity = 3.2–3.265. Hardness = 4. Colour and streak, lavender-blue to leek-green. Opaque. Fibres somewhat elastic. Melts easily before the blow-pipe to a black, shining, opaque, somewhat frothy glass, attracted by the magnet. Single fibres melt in the flame of a spirit-lamp. With borax it forms a green transparent bead, changing to brown on addition of nitre.

Analyses: *a.* from Africa, by Klaproth (Beitr. vii. 237); *b.* from Africa, by Stromeyer (Pogg. Ann. xxiii. 153); *c.* from Wakenbach, by Delesse (Ann. Min. [3] x. 307).

	SiO <sup>2</sup>	Fe <sup>2</sup> O	MnO	Mg <sup>2</sup> O	Cu <sup>2</sup> O	Na <sup>2</sup> O	K <sup>2</sup> O	H <sup>2</sup> O	Cl	P <sup>2</sup> O <sup>5</sup>
<i>a.</i>	50.0	40.5	—	—	1.5	5.0	—	3.0	—	—
<i>b.</i>	51.22	34.08	0.10	2.48	0.03	7.07	—	4.80	—	—
<i>c.</i>	53.02	25.62	0.50	10.14	1.10	5.69	0.39	2.62	0.51	0.17

From these analyses, Rammelsberg (*Mineralchemie*, p. 476) deduces the formula  $7M^{2}O.9SiO^{2} + (1\frac{1}{2} \dots 3)H^{2}O$ . Taking the larger amount of water, and supposing 2 at. to be basic, this formula may be reduced to  $(M^{1}H^{1})Si^{2}O^{27} + aq.$ , or  $9R^{2}SiO^{3} + aq.$ , which is the formula of a metasilicate. The mineral is perhaps formed from soda-hornblende (arfvedsonite), by abstraction of lime.

A somewhat similar mineral occurs at Stavern in Norway.

**CROCOISITE.** Native chromate of lead (i. 934).

**CROCONIC ACID.**  $C^{8}H^{2}O^{8} = (C^{8}O^{8}) \cdot H^{2}O^{2}$ .—(L. Gmelin [1825], Pogg. Ann. iv. 37; Handbook, x. 388. Liebig, Pogg. Ann. xxxiii. 90. Heller, J. pr. Chem. xii. 230; Ann. Ch. Pharm. xxiv. 1; xxxiv. 232. Will, Ann. Ch. Pharm. cxviii. 177.)

When the compound of carbonic oxide and potassium, obtained by passing the dry gas over melted potassium,—or, as a secondary product, in the preparation of potassium by heating carbonate of potassium with charcoal—is immersed in water, inflammable gas is evolved, and a strongly alkaline yellowish-red solution is formed, which, when left to evaporate at a gentle heat, becomes pale yellow and deposits long yellow needles of croconate of potassium, while oxalate of potassium remains in the mother-liquor. These two salts are not, however, the immediate products of the action of air and water on the compound of potassium and carbonic oxide, their formation being preceded by that of a red salt, the rhodizonate of potassium, the solution of which decomposes, during evaporation, into croconate, oxalate, and probably also carbonate of potassium. The relations between these several products are not exactly known.

The black mass produced in the preparation of potassium should be exposed to the air for several weeks before it is dissolved in water; it then gradually acquires a red or yellow colour and dissolves in water without explosion; but if it has been exposed to the air for a few hours only, it takes fire in contact with water (because it contains free potassium), and produces a violent explosion which shatters the vessel.

Croconic acid is obtained in the free state by digesting the potassium-salt with a mixture of sulphuric acid and absolute alcohol for several hours, then filtering, and leaving the solution to evaporate.

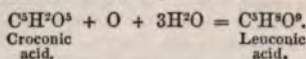
It cannot be conveniently prepared by decomposing the lead-salt with sulphuric acid, as the decomposition is never complete, or by decomposing the lead or copper salt with sulphuretted hydrogen, as in that case peculiar sulphur-compounds are formed which are troublesome to separate.

Croconic acid crystallises in anhydrous, orange-yellow, transparent prisms and granules (Gmelin); in golden-yellow laminæ or granular crystals containing  $C^{8}H^{2}O^{8} + 3H^{2}O$ , which become opaque and crumble to a yellow powder when left over oil of vitriol, and more quickly when heated to 100° C. (Will). It is inodorous, has a strongly acid taste, and reddens litmus. It dissolves easily in water,

forming a yellow solution, which gradually becomes colourless; easily also in *alcohol*. (Gmelin.)

Croconic acid is not altered by a temperature of  $180^{\circ}\text{C}$ ., but when more strongly heated, it gives off white and yellow irritating vapours and leaves a small quantity of easily combustible charcoal. In combination with potash it is quickly decomposed by *permanganate of potassium* in presence of sulphuric acid, being entirely converted into carbonic acid. (Will)

The solution of the potassium-salt is completely decolorised by *nitric acid* and by *chlorine* (Gmelin, Liebig), with evolution of nitric oxide free from carbonic acid in the former case (Gmelin, Will), without evolution of gas in the latter (Will). In both cases a new acid, leuconic acid, is produced:



The croconates,  $\text{C}^5\text{MPO}^5$ , are yellow (hence the name of the acid). Many of them are anhydrous (Will). They decompose below a red heat, with glowing and sparking, giving off carbonic oxide and carbonic anhydride, and leaving a mixture of charcoal and metallic oxide, carbonate or metal. They withstand the action of air and light, even their aqueous solutions not being altered by exposure to the air. The croconates of the alkali-metals and some others are soluble in water; they all dissolve with decomposition in nitric acid (*vid. sup.*) Some of the croconates of the heavy metals are soluble in *alcohol* and *ether*. (Heller.)

*Croconate of Aluminium*.—Yellow crystals easily soluble in water and alcohol. (Heller.)

*Croconate of Ammonium*.—Reddish-yellow needles soluble in water and alcohol. (Heller.)

*Croconates of Antimony*.—Croconate of potassium added to a solution of trichloride of antimony in hydrochloric acid forms a lemon-yellow precipitate, soluble in excess of chloride of antimony. (Gmelin.)

*Croconate of Barium*,  $2\text{C}^5\text{Ba}^2\text{O}^5 + 3\text{H}^2\text{O}$  (Will).—Yellow pulverulent precipitate, insoluble in water and in alcohol (Gmelin). Does not give off its water at  $200^{\circ}\text{C}$ . (Will)

*Croconate of Bismuth*.—Lemon-yellow precipitate soluble in excess of nitrate of bismuth (Gmelin). Contains 55.68 per cent.  $\text{Bi}^2\text{O}^3$ . (Heller.)

*Croconate of Cadmium*.—Yellow pulverulent precipitate, somewhat soluble in water and alcohol. (Heller.)

*Croconate of Calcium*.—Lemon-yellow crystals sparingly soluble in water and alcohol (Gmelin). They contain  $\text{C}^5\text{Ca}^2\text{O}^5 + 3\text{H}^2\text{O}$ , and give off their water completely at  $160^{\circ}\text{C}$ . (Will)

*Croconate of Cobalt*.—The potassium-salt mixed with an aqueous cobalt-salt yields, after a few hours, dark-brown transparent crystals, with beautiful violet reflex; soluble in water and alcohol. (Heller.)

*Croconate of Copper*,  $\text{C}^5\text{Cu}^2\text{O}^5 + 3\text{H}^2\text{O}$ , is deposited in prismatic crystals on mixing the hot solutions of croconate of potassium and cupric chloride. The crystals belong to the trimetric system. Dominant form,  $\infty\text{P}$ , with the faces  $\infty\text{P}\infty$ . Inclination of  $\infty\text{P}$ :  $\infty\text{P}$  in the brachydiagonal principal section =  $108^{\circ}$ . Cleavage parallel to  $\infty\text{P}$ . The crystals have a fine deep blue colour by reflected light, and appear orange-coloured by transmitted light. They give off 13.8 per cent. (= 2 at.) water at  $100^{\circ}\text{C}$ ., the remaining atom not being given off till the salt is heated to a temperature at which it undergoes complete decomposition, giving off carbonic oxide and carbonic anhydride, yielding an acid distillate, the latter portions of which form a black precipitate with nitrate of silver, and leaving a residue of copper and charcoal. The salt, heated in the air to a temperature below redness, burns with a glimmering light and slight sparkling, leaving first a red powder of metallic copper, afterwards cupric oxide. Fuming nitric acid sets it on fire with vivid sparkling.

Croconate of copper dissolves very sparingly in cold water, rather more in boiling water, forming an acid solution, which forms with potash a blue precipitate soluble in excess of the alkali. *Ammonia* produces a similar reaction, and likewise dissolves the crystals. The aqueous solution forms but a slight deposit of copper upon *iron*, unless hydrochloric acid is also present. (Gmelin.)

*Croconates of Iron*.—Croconate of potassium forms with aqueous *ferric* chloride a clear black mixture, which in thin layers exhibits a garnet-red colour (Gmelin): it deposits indistinct, very dark-coloured crystals, soluble in water and alcohol (Heller). The potassium-salt, added to *ferrous* sulphate forms a dark yellowish



liquid, which afterwards deposits brown flakes, changing, after some hours, to dark brown crystals, blue by reflected light; they resemble the copper-salt in form, and are soluble in water and alcohol. (Heller.)

*Croconate of Lead.*— $\text{C}^2\text{Pb}^2\text{O}^3 + 2\text{H}^2\text{O}$  (Will), is obtained by pouring, first acetic acid, then a hot dilute solution of acetate of lead, into a solution of croconate of potassium. It is a micaceous, golden-yellow precipitate, which gives off its water at  $180^\circ\text{C}$ . (Will.)

*Croconate of Magnesium.*—Dark brown prisms. (Heller.)

*Croconate of Manganese.*—By evaporating the acid with manganous acetate, or leaving the potassium-salt for some time in contact with manganous sulphate, dingy yellow crystals are obtained, having a faint blue reflex. (Heller.)

*Croconate of Mercury.*—The potassium-salt added either to mercuric or mercurous nitrate, forms a yellow precipitate.

*Croconate of Nickel.*—By evaporating croconic acid with sulphate of nickel, light brown grains are obtained, soluble in water and alcohol. (Heller.)

*Croconates of Potassium.* *a. Neutral,*  $\text{C}^2\text{K}^2\text{O}^3 + 2\text{H}^2\text{O}$ .—Prepared by cautiously dissolving in water the black mass obtained as an accessory product in the preparation of potassium,—filtering,—concentrating the filtrate over the water-bath, and leaving it to crystallise,—pressing the yellow needles thus obtained,—and recrystallising from hot water (Gmelin). Crystallises in slender needles or prisms of an orange yellow colour, which effloresce and give off their water at a temperature considerably below  $100^\circ\text{C}$ ., or when treated with oil of vitriol, and become lemon-yellow. At a high temperature the salt carbonises. Nitric acid and chlorine decolorise it, and convert it into leuconate of potassium (p. 108). It is moderately soluble in water, especially in hot water; insoluble in absolute alcohol. The aqueous solution reduces chloride of gold when heated with it; with mercuric chloride it forms, after a while, a white precipitate, probably consisting of calomel.

*b. Acid salt,*  $\text{C}^2\text{HKO}.\text{C}^2\text{H}^2\text{O}^3 + 2\text{H}^2\text{O}$ .—Obtained by adding to a solution of the neutral salt, a quantity of sulphuric acid, not sufficient to decompose it completely. Forms prisms more deeply coloured than the neutral salt, and having an acid reaction. (Gmelin.)

*Croconate of Silver,*  $\text{C}^2\text{Ag}^2\text{O}^3$ , is precipitated in aurora-red flakes, insoluble in water.

*Croconate of Sodium,* obtained by neutralising the acid with carbonate of sodium, forms rhomboïdal prisms less deeply coloured than the potassium-salt, and containing water of crystallisation. Very soluble in water, sparingly in alcohol. (Heller.)

*Croconate of Tin.*—The potassium-salt, added to a solution of stannous chloride throws down a large quantity of an orange-yellow powder (Gmelin); it decomposes, with violence when heated, and is sparingly soluble in water (Heller). *Stannic chloride* is not precipitated by croconate of potassium.

*Croconate of Uranium.*—The hyacinth-red mixture of croconic acid or croconate of potassium with uranic nitrate yields, by spontaneous evaporation, yellowish-red, transparent crystals, easily soluble in water and in alcohol. (Heller.)

*Croconate of Zinc.*—Crystalline grains soluble in water and alcohol.

*Croconate of Zirconium.*—Yellow crystals soluble in water and alcohol. (Heller.)

**CROCOXANTHIN.** A peculiar yellow colouring matter, said to exist pure in the flowers of *Crocus luteus*, mixed with other substances in the stigmata of *Crocus sativus* and *Crocus multifidus*, and in other plants. It is a golden-yellow amorphous body, of considerable colouring power, easily soluble in water and alcohol, but insoluble in ether. It is not altered either by acids or by bases,—a character which distinguishes it from other yellow colouring matters, such as xanthin, &c.; forms yellow lakes with several metallic oxides, and may be fixed on tissues. (Filhol, J. Pharm. [3] xlvi.)

**CROCUS.** A term applied by the older chemists to many metallic compounds; thus, oxysulphide of antimony (i. 328) was called *Crocus Antimonii*, or *Crocus metallorum*; sesquioxide of iron, *Crocus Martis* and *Crocus Martis operitivus*: cuprous oxide, *Crocus Veneris*, &c.

**CROCUS SATIVUS.** See SAFFRON.

**CRONSTEDTITE.** *Chloromelan.*—A hydrated ferrous silicate, containing also small quantities of magnesia and manganese, found in a vein of silver ore at Příbram in Bohemia, accompanying pyrite, siderite, calcite, and limonite; also at Wheal Maudlin in Cornwall, with pyrite and siderite. It crystallises in the hexagonal system, forming six-sided prisms, with the basic terminal face, generally in diverging groups; also

reniform and amorphous. Cleavage basal, very distinct. Colour raven-black. Streak dark-green. Opaque, with strong vitreous lustre. Rather brittle; thin laminae, somewhat flexible. Specific gravity = 3.3 to 3.4. Hardness = 2.5. Before the blowpipe it swells up a little, and melts on the edges to a blackish-grey magnetic slag. With borax and phosphorus-salt it gives the reactions of iron, silica, and manganese; with soda, that of manganese. It gives off water when heated in a test-tube. Decomposed by hydrochloric or sulphuric acid, forming a jelly of silica.

Analysis, by Kobell (Schw. J. lxii. 199):

SiO <sup>2</sup>	Fe <sup>2</sup> O	Fe <sup>4</sup> O <sup>3</sup>	Mg <sup>2</sup> O	Mn <sup>2</sup> O	H <sup>2</sup> O
22.45	27.18	35.35	2.88	5.08	10.70 = 103.64,

agreeing approximately with the formula  $3(2\text{Fe}^2\text{O} \cdot \text{SiO}_2) \cdot 2(\text{Fe}^4\text{O}^3 \cdot 3\text{H}^2\text{O})$ , or  $3\text{Fe}^4\text{SiO}^4 + 4(\text{Fe}^2)^m\text{H}^2\text{O}^4$ .

**CROSS-STONE** or **CRUCITE**. Syn. with **CHIASTOLITE** (i. 868).

**CROTON OIL.** *Oleum crotonis*.—A fatty oil existing, to the amount of about 50 per cent. in the seeds of *Croton Tiglium*, a plant of the Euphorbiaceae order. It is usually obtained by strongly pressing the bruised seeds between hot plates, —sometimes by digestion with alcohol or sulphide of carbon.

The properties of croton oil differ to a certain extent according to the mode of preparation. The oil obtained by pressure has a more or less yellow or brown colour, and a peculiar rancid odour; its taste is mild at first, but afterwards burning. It is somewhat viscid, especially when old, and deposits more or less of a dirty white body. It is a powerful drastic purgative, and irritates and reddens the skin. The latter property is due to a peculiar oily body, called *crotonol*,  $\text{C}^6\text{H}^{14}\text{O}^2$ . The purgative action was formerly ascribed to a volatile acid of the oleic series, *crotonic acid*; but subsequent investigations have shown that this is not the case; the exact nature of the purgative principle is not known. According to Mayer (N. Jahrb. pr. Pharm. x. 318), a volatile, highly irritating substance, which affects the lining membranes of the nose and mouth, is evolved during the pressing of croton seeds between warm plates; this substance also remains to be investigated.

Brandes, who first examined croton oil, supposed that it contained a small quantity of an alkaloid, to which he gave the name *crotonine*; he obtained it by digesting the alcoholic extract of croton seeds with water and magnesia. According to Weppen, however, this supposed alkaloid is nothing but a magnesia-soap of croton oil.

The most exact investigation of croton oil has been made by Th. Schlippe (Ann. Ch. Pharm. cv. 1). To obtain the oil, the seeds were first pressed between warm plates, and the remaining cake, after being comminuted, was exhausted with alcohol of 85 per cent. in a displacement apparatus, so arranged that the alcohol which ran off could be distilled back again. After this process had been repeated four times, the receiver contained two layers of liquid, the lower of which was oily, and contained 14 pts. oil to 1 pt. alcohol, the upper mobile, containing 23 pts. alcohol to 1 pt. oil. The residual mass, still saturated with alcohol, was pressed, and yielded a considerable quantity of oil surmounted by a layer of alcohol. From this and the preceding portions the alcohol was distilled off. In this manner four portions of oil were obtained. (1.) The portion obtained by warm pressure; (2.) That which was displaced and dissolved by the alcohol; (3.) That displaced by the alcohol but not dissolved, forming the lower layer above mentioned; (4.) The portion expressed from the residue. Of these the second exerted the strongest irritating action on the skin; this action was much weaker in the third, and weakest in the first and fourth.

Croton-oil obtained by pressure was found to contain stearic, palmitic, myristic, and lauric acids, two acids of the oleic series, whose formulæ lay between  $\text{C}^{17}\text{H}^{32}\text{O}^2$  and  $\text{C}^{16}\text{H}^{30}\text{O}^2$ , —also crotonic and angelic acids, together with glycerin and other substances.

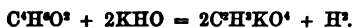
The alcoholic extract of croton-seeds, diluted with water and evaporated to remove the alcohol, became turbid on cooling, and deposited a dirty yellow crystalline body, which has not been further examined, but is perhaps the purgative principle of the seeds. This body is decomposed during the saponification of croton oil, and yields a peculiar black resin (*vid. sup.*)

**CROTONIC ACID.**  $\text{C}^6\text{H}^8\text{O}^2 = \text{C}^6\text{H}^8\text{O} \cdot \text{H} \cdot \text{O}$ , or  $\text{C}^6\text{H}^8\text{O}^4$ . (Pelletier and Caventou, J. Pharm. iv. 289. —Caventou, *ibid.* xi. 110. —Buchner, Repert. Pharm. xix. 185. —Schlippe, Ann. Ch. Pharm. cv. 1.)—This acid, which belongs to the oleic series,  $\text{C}^6\text{H}^{2n-2}\text{O}^2$ , and occupies the intermediate place between acrylic acid  $\text{C}^3\text{H}^4\text{O}^2$ , and angelic acid,  $\text{C}^4\text{H}^6\text{O}^2$ , is obtained by the saponification of croton oil. The oil extracted by pressure is saponified with soda-ley; the alkaline liquid is treated with common salt, which separates a soap containing palmitate, stearate, myristate, and laurate of sodium, leaving crotonate and angelate in solution; this soap is washed



with brine; and the mother-liquor, together with the washings, is supersaturated with tartaric acid. It then becomes colourless and deposits yellow flocks,—a product of the decomposition of the supposed purgative principle mentioned in the last article,—which cake together to a black resin. The filtered liquid is then distilled; the distillate, containing crotonic, angelic, and hydrochloric acid, is neutralised with baryta, and evaporated to dryness; and the residue is again distilled with dilute tartaric acid. Crotonic acid then distils over first, together with water, and afterwards angelic acid crystallises in the neck of the retort. The saturation of the liquid distillate with baryta, and the decomposition by tartaric acid, are repeated till the distillate no longer contains hydrochloric acid; the liquid is then finally neutralised with baryta; the excess of baryta removed by carbonic acid; the filtrate evaporated to dryness; and the residue decomposed by heating it with strong phosphoric acid. As the liquid cools, the crotonic acid rises to the surface, and may be separated by means of a pipette.

Crotonic acid is a colourless, oily liquid, having a somewhat pungent odour and an acid taste. It dissolves with moderate facility in pure water, but is insoluble in saline water. When carefully heated with *hydrate of potassium*, it gives off hydrogen, and forms acetate of potassium:



The *crotonates* are odorless. The *potassium-salt* forms rhomboidal prisms, permanent in the air, sparingly soluble in alcohol of specific gravity 0.86. The *barium-salt* is very soluble in water and in alcohol, and separates by concentration in nacreous crystals, the powder of which excites powerful irritation in the throat. The *magnesium-salt* is granular and sparingly soluble in water.

Crotonate of ammonium forms a cream-coloured precipitate with *ferrous sulphate*; white with *silver* and *lead salts*; bluish-white with salts of *copper*. It does not precipitate ferric sulphate or chloride of mercury.

**CROTONOL.**  $C^9H^{10}O^2$ . (Th. Schlippe, Ann. Ch. Pharm. cv. 1.)—Contained in croton oil. To prepare it, the oil is shaken up with a quantity of alcoholic soda sufficient to form a milk; the mixture is gently heated for some hours; water or brine is added; and the oily layer which then rises to the surface, is completely removed by repeated filtration through wet filters. On mixing the filtrate with water and hydrochloric acid, another oil separates out, which is dissolved in cold alcohol, digested with hydrate of lead, till its acid reaction is neutralised (whereby a flocculent precipitate is formed which afterwards coagulates into a greasy mass), then mixed with a little soda and a large quantity of water. The milky liquid thereby produced becomes clear after a while and deposits an oil, which is to be washed with water, then dissolved in ether, and the ethereal solution again washed with water, and evaporated in vacuo. It then leaves crotonol amounting to 4 per cent. of the oil.

Crotonol forms a colourless or faintly yellow viscid mass of the consistence of turpentine. It has a faint peculiar odour, and is the part of croton-oil which irritates the skin, not the purgative principle.

It cannot be distilled without decomposition, even in vacuo or in a stream of carbonic acid gas. When distilled with water, either pure or containing sulphuric acid, it yields first a colourless, then a black oil, which cannot be distilled at 200° even in vacuo, and leaves a black resin which forms with alcohol a turbid solution precipitable by acetate of lead. A solution of crotonol in absolute alcohol does not form crystals with *ammonia*. Crotonol does not combine with acid *sulphite of sodium*. With melting *sodium* it gives off gas with violence, then becomes thicker and resinous. By boiling with caustic *potash* or *soda*, it forms a brown resin which no longer reddens the skin. The alcoholic solution of crotonol does not precipitate metallic salts.

**CROUPI OIL.** *Toloucina oil*.—A fatty oil obtained from the seeds of *Carapa Toloucina*, a tree twenty feet high, growing on the Gold Coast. The seeds are first dried and smoked, then bruised, boiled with water, and the oil which separates is collected. The oil has a bitter taste, apparently due to the presence of a foreign basic substance, and a repulsive odour; it dissolves completely in ether, but is separated by alcohol into two parts, the solid portion, together with the basic substance, dissolving, while a liquid oil remains undissolved. Croupi oil is used by the natives of the West Coast of Africa for burning, and as a remedy against intestinal worms. (Handw. d. Chem. 2<sup>te</sup> Aufl. ii. [3] 231.)

**CROWN GLASS.** See GLASS.

**CRUCILITE.** See STAUROLITE.

**CRUCITE.** Syn. of CHIASTOLITE (i. 868).

**CRUSTACEA.** The shells of crustacea contain organic and inorganic matter in  
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nearly equal quantities, the inorganic portion consisting mainly of carbonate of calcium with a smaller quantity of phosphate. Fremy (Ann. Ch. Phys. [3] xliii. 47) found in the shell:

	Ca <sup>2</sup> PO <sup>4</sup> .	Ca <sup>2</sup> CO <sup>3</sup> .	Organic matter.
Of the sea-crab . . .	6.7	49.0	44.3
Of the land-crab . . .	6.7	56.8	36.5

The organic portion consists mainly of chitin (i. 874.)

**CRYOLITE.** Native fluoride of sodium and aluminium,  $3\text{NaF} \cdot \text{AlF}_3$ . Found in large quantity at Evgtok, in the Arksut-fjord, in West Greenland, where it forms a bed 80 feet thick and 300 feet long; also, with chiolite, lithia-mica and fluor spar, at Miask, in the Ural. Crystallises in the dimetric system. Specific gravity = 2.9—3.08. Hardness = 2.5. Colourless and transparent when pure. At the surface of the bed just mentioned, the mineral is white, but below the surface it exhibits a continually darker colour, and at last almost black: the colour is, however, destroyed by a moderate heat. Cryolite melts below a red heat and forms an opaque glass on cooling. It is very slightly soluble in water. It is used for the extraction of aluminium, and also for the preparation of caustic soda for soap-boiling. (See ALUMINIUM, i. 157.)

**CRYPTIDINE.**  $\text{C}^{11}\text{H}^{11}\text{N}$ . An organic base contained in that portion of the bases from coal-tar (*q. v.*) which possesses the highest boiling point (above  $274^\circ \text{C}$ ). It has not been obtained pure, its composition having been determined only by the analysis of the platinum-salt, which crystallises in yellow needles. It is homologous with chinoline,  $\text{C}^8\text{H}^8\text{N}$ , and lepidine,  $\text{C}^{10}\text{H}^9\text{N}$ . (C. Gr. Williams, Chem. Gaz. 1856, 283.)

**CRYPTOLIN.** An organic liquid, found together with brewstolin (i. 663) in cavities of topaz, chrysoberyl, quartz-crystals from Quebec, and amethyst from Siberia. The two liquids sometimes occur in the same cavities, but they are not miscible. Cryptolin, when exposed to the air, speedily hardens into a yellowish, transparent, resinous body, not volatilisable by heat, or soluble in alcohol or in water, but dissolving rapidly and with effervescence in sulphuric acid. Nitric and hydrochloric acid also dissolve it. Index of refraction nearly the same as that of water. (Dana, ii. 471.)

**CRYPTOLITE** (from *κρυπτος*, concealed). Native phosphate of cerium,  $\text{CePO}_4$ , discovered by Wöhler (Ann. Ch. Pharm. lvii. 268) in the rose-coloured apatite of Arendal in Norway, from which it is separated by dissolving the apatite in nitric acid, the cryptolite then remaining undissolved, in very small hexagonal crystals. (See PHOSPHATES.)

**CRYSTALLIN**, or *Globulin*. An albuminous substance, contained in the crystalline lens of the eye, and supposed by Berzelius to be identical with the albuminous constituent of the blood-corpuscles. (See GLOBULIN.)

**CRYSTALLINE.** An old name for aniline or phenylamine.

**CRYSTALLISATION.** A crystal is a solid body, bounded by plane surfaces, disposed according to a regular law of symmetry, the form thus produced being essentially related to the composition and properties of the body, so that the minutest particles into which the body can be mechanically divided exhibit either the same form, or one related to it by determinate laws. This essential connection between form and composition distinguishes a crystal from a regular form artificially produced, as by carving or modelling. All crystals cleave in certain directions more easily than in others, and all, excepting those which belong to the regular system (see CRYSTALLOGRAPHY), refract light doubly.

To enable a body to assume the crystalline state, its particles must possess a certain freedom of motion: hence, the fluid state is for the most part, an essential preliminary to crystallisation. Sometimes, indeed, an amorphous solid—that is to say, one which has no definite structure, either crystalline or organised—passes spontaneously into the crystalline state without previous liquefaction. This is the case with plastic sulphur, vitreous arsenious acid, and barley-sugar, which gradually change from transparent amorphous solids to opaque aggregates of minute crystals. But generally speaking it is in the passage of a body from the liquid or gaseous to the solid state that the regular and symmetrical arrangement of the molecules takes place, which constitutes crystallisation. The vapours of many substances, when they come in contact with cold surfaces pass at once to the state of crystalline solids, *e. g.* sulphur, iodine, benzoic acid, arsenious acid, camphor, &c. It is, however, in the transition from the liquid to the solid state that crystallisation most frequently takes place. If the body has been brought into the liquid state by the action of heat alone, it may be made to crystallise by cooling, *e. g.* bismuth, sulphur. To obtain definite crystals in this manner, the liquid mass is allowed to cool only till a certain portion near the surface and in contact with the sides of the vessel has become solid, a hole being then pierced in the crust,



and the vessel inverted, so that the portion which still remains liquid may run out (i. 590). \* A solid body dissolved to saturation in a hot liquid may also be made to crystallise by cooling; *e. g.* sulphur from solution in sulphide of carbon; nitre or alum from solution in water. The crystallisation of a solid from solution may likewise be effected by removing the solvent, either by evaporation, or by adding another substance with which the solvent has a greater tendency to unite than with the substance previously dissolved in it; in this manner, chloride of sodium crystallises from its aqueous solution on addition of chloride of calcium; nitre from its aqueous solution on addition of alcohol; iodine from solution in hydriodic acid on the introduction of a small quantity of chlorine.

The more slowly the liquefied body is brought back to the solid state, and the more the liquid is kept at rest, the smaller is the number and the greater the size and regularity of the crystals; but if the solvent be cooled or separated quickly, the crystals are numerous but small and ill defined. In the former case, the particles of the solidifying body have time to unite themselves regularly with those which separate first from the fluid and form nuclei of crystallisation; if, on the contrary, the crystallisation takes place rapidly, a great number of particles solidify at the same time, each forming a nucleus to which other portions may attach themselves, and thus we obtain a number of crystals irregularly formed and interlacing each other in all directions. In this consists the difference between sugar-candy and loaf-sugar; similarly, all granular and fibrous bodies, such as tufa and fibrous gypsum, must be regarded as collections of imperfectly formed crystals. To obtain crystals as large and regular as possible, Leblanc recommends (*J. Phys.* lv. 300) to allow a solution not quite saturated to cool slowly, so that none but distinct crystals may be formed, then to pick out the best formed of these and lay them, separate from one another, in a solution of the same salt, which by gentle warming in contact with the salt has been made to hold in solution a quantity of it just a little greater than that which it can contain at the ordinary temperature, so that it may deposit this excess on the crystals laid in it. This treatment is repeated till the crystals have obtained the desired magnitude, care being taken to turn them frequently, because the surfaces resting on the bottom are in a less favourable position than the others for taking up fresh particles. The trouble of repeatedly preparing a slightly supersaturated solution may be saved by suspending in the upper part of the liquid a quantity of the salt contained in a bag of muslin or in a funnel. Irregularly developed crystals may also be brought to regular shape by covering the fully developed surfaces with wax, so that only the faces which require further development may come in contact with the solution.

The formation of crystals takes place most readily in contact with bodies which abstract heat from the liquid, or to which the crystals can adhere. Hence they form on the surface of the liquid, in so far as evaporation and cooling by the influence of the air, or adhesion of the air to the crystals, can give rise to their production; also on the bottoms and sides of the containing vessels, and on solid bodies immersed in the liquid. For the most part, crystals deposit themselves more easily on wood and string than on porcelain, glass, and metal; more easily on porcelain than on glass, and generally more easily on rough than on smooth surfaces, because the former present a greater number of points of adhesion. When a glass tube containing a crystallisable liquid is scratched with a glass rod, the crystals deposit themselves in preference on the scratches. Crystallisation is also especially facilitated by introducing into the liquid a crystal of the substances previously formed. A solution saturated at a high temperature may, under certain circumstances, be cooled down several degrees without depositing crystals; but the introduction of a crystal of the substance, causes the whole to solidify instantly in a crystalline mass. This phenomenon is easily exhibited with Glauber's salt. (See SOLUTIONS, SUPERSATURATED.) In like manner, the introduction of a crystal of nitre into a solution of nitre and Glauber's salt, prepared hot and subsequently cooled, causes the nitre to separate alone; a crystal of Glauber's salt removes only the Glauber's salt; whereas, if the solution be left to itself, both salts crystallise out together, the crystals interlacing each other. (Lowitz.)

When a solution evaporates below its boiling-point, the first crystals are usually deposited on the sides of the vessel at the uppermost surface of the liquid: another portion of the liquid often rises through these, and yields by evaporation new crystals, which ultimately make their way over the edge of the vessel. This is efflorescence. When crystals form at the bottom of a liquid, a current is produced, because the individual crystals take, from that part of the solution with which they are immediately in contact, as much of the salt as is possible under the existing circumstances; consequently this part of the liquid becomes lighter and rises to the surface, its place being supplied by a more saturated portion of the liquid.

When a body crystallises from solution in a liquid, and the latter is not completely removed by evaporation, there remains a portion called the mother-liquor (*Eau*



*mère, Mutterlaugé*). This liquid holds in solution as much of the crystallising body as is consistent with its quantity and temperature. It often happens, especially when crystallisation proceeds rapidly, and the crystalline laminæ in the act of uniting leave small spaces between them, that small and (even with regard to the same substance) very variable quantities of the mother-liquid remain enclosed in the crystalline mass, forming the Water of Decrepitation. Crystals which contain liquids thus enclosed, and do not melt below the boiling-point of the mother-liquid, exhibit, when heated, the phenomena of Decrepitation, the vapour given off from the mother-liquid bursting the crystalline mass with violence. This water of decrepitation, which, as an accidental mechanical admixture, has no influence on the form of the crystal, is altogether different from the chemically-combined water which certain crystals contain in definite proportion, and which is essential to their crystalline form. Common salt, crystallised by slow evaporation from an aqueous solution does not decrepitate; but when crystallised by rapid boiling of the liquid, it decrepitates violently. Many forms of calcespar decrepitate, others do not.

If a solution, in addition to the crystallising substance, likewise contains others which are less easily crystallisable, the latter will remain in the mother-liquid after the separation of the greater part of the former. This circumstance furnishes a method of purifying easily crystallisable substances by repeated solution, crystallisation, pouring off of the mother-liquid, washing with small quantities of the cold solvent, and pressing between blotting-paper. In this method of purification, the formation of large crystals by slow cooling or evaporation is usually preferred, because they present fewer surfaces, and are therefore more easily freed by washing from the adhering mother-liquid. Sometimes, on the contrary, as in the French method of purifying saltpetre, the smallest possible crystals are formed by constant stirring and rapid cooling of the hot solution, because large crystals of this salt contain a greater quantity of mechanically included mother-liquor, which cannot be removed by washing.

It has already been stated that the crystalline form of a body bears an essential relation to its nature and composition. Accordingly we find that every substance crystallises either in one single form or in a number of forms related to each other by simple laws and derivable one from the other; in other words belonging to the same crystalline system (see CRYSTALLOGRAPHY). Many bodies, however, both simple and compound, crystallise in two or more forms belonging to different crystalline systems, and not derivable one from the other; such bodies are said to be dimorphous, trimorphous, or generally polymorphous. (See DIMORPHISM.)

On the other hand, different substances often crystallise in forms either identical or exhibiting only small differences in the inclinations of the corresponding planes. When the forms are exactly similar, the substances are said to be isomorphous, when small differences in the angles exist, they are called homeomorphous. Isomorphous or homeomorphous compounds exhibit perfect similarity of chemical composition: thus, the alums, which crystallise in regular octahedrons and allied forms are, all composed according to the general formula  $\left\{ \begin{smallmatrix} M \\ (R^2)^m \end{smallmatrix} \right\} 2SO^4 + 12 \text{ aq.}$ , where M denotes a monatomic metal, like potassium, and R a sesquiatomic metal, like aluminium; the magnesian double sulphates, which crystallise homeomorphously in the monoclinic system, are all composed analogously to sulphate of magnesium and potassium  $(KMg)SO^4 + 3 \text{ aq.}$  Isomorphous salts are capable of crystallising together in any proportion; in other words, the isomorphous elements which enter into them are capable of replacing one another in any proportion; thus, common alum  $\left\{ \begin{smallmatrix} K \\ (Al^2)^m \end{smallmatrix} \right\} 2SO^4 + 12 \text{ aq.}$  and iron-alum,  $\left\{ \begin{smallmatrix} K \\ (Fe^2)^m \end{smallmatrix} \right\} 2SO^4 + 12 \text{ aq.}$ , can crystallise together in all proportions; hence it is difficult to purify common alum from iron by crystallisation. (See ISOMORPHISM.)

**CRYSTALLOGRAPHY** is the science which treats of the external forms of crystals, and of the laws of symmetry according to which their faces are disposed.

Crystals are bounded by plane faces. The straight line in which two contiguous faces intersect is called an edge; the point in which three or more faces intersect is called an angle, solid angle, or summit of the crystal.

**Similar and Dissimilar Boundaries.** Similar faces of a crystal are those which resemble each other in form and in relative position; dissimilar, those which differ in either respect. Similar edges are those which are formed by similarly situated faces meeting at equal angles. Similar angles or summits are those which are formed by the concurrence of similar faces and edges; angles are also distinguished as three-faced, four-faced, &c., according to the number of faces by which they are formed. The regular octahedron (*fig. 149*), and the cube (*fig. 150*), have all their faces, edges and angles similar; the rhombic dodecahedron (*fig. 151*) has all its faces



Fig. 149.

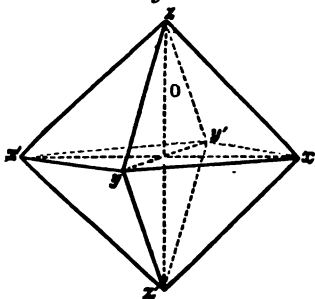
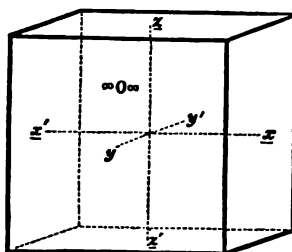


Fig. 150.



and edges similar; but its solid angles are of two kinds, viz. eight 3-faced and six 4-faced angles. The square prism with pyramidal summits (fig. 152) has dissimilar

Fig. 151.

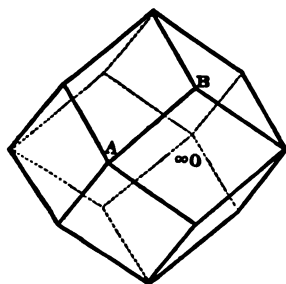
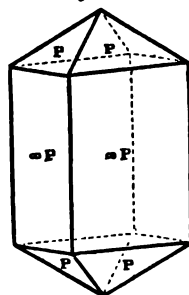


Fig. 152.



faces, triangular and rectangular; dissimilar edges, viz. 1, those formed by the intersection of two triangular faces; 2, those formed by two rectangular faces; and 3, those formed by a triangular and a rectangular face; and dissimilar angles or summits, viz. two at the extremities of the vertical axis, formed by the concurrence of four similar triangular faces; and eight others, also four-faced, but formed by the intersection of dissimilar faces and edges. Angles are also spoken of as equal- or unequal-edged, according as the edges which meet in them are similar or dissimilar. An unequal-edged angle may also be symmetrical or unsymmetrical, according as the dissimilar edges which form it follow one another in regular order or not. The four-edged angles of the double six-sided pyramid (fig. 153) are symmetrical, but those of the six-sided prism with pyramidal summits (fig. 154) are unsymmetrical.

Fig. 153.

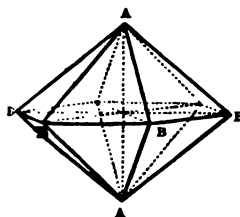


Fig. 154.

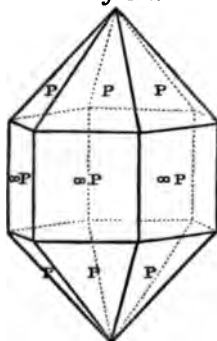
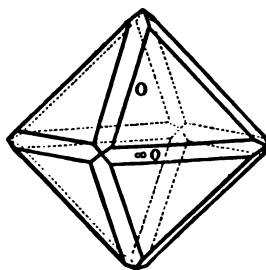


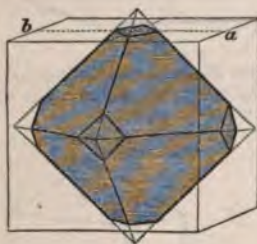
Fig. 155.



**Simple and Complex forms (Combinations).** Simple forms are those which contain only similar faces, *e. g.* the regular octahedron, cube, and rhombic dodecahedron (figs. 149, 150, 151). Complex forms, or combinations, are those in

which dissimilar faces occur (*e. g.* *figs.* 152, 154). A combination is made up of those simple forms which would result from the extension of one set of similar faces till the others disappear; thus (*fig.* 155) is a combination of the octahedron  $O$ , and the rhombic dodecahedron  $\infty O$ . If we suppose the  $O$ -faces to be extended till they meet, the  $\infty O$ -faces will disappear and the octahedron (*fig.* 149) will result; conversely the extension of the faces  $\infty O$  to the obliteration of the others produces the dodecahedron (*fig.* 151).

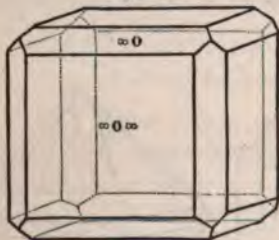
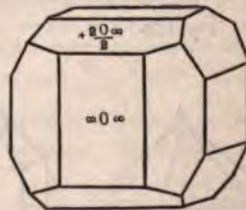
The relation of a complex form to the simple forms of which it is made up may also be represented as follows:—Suppose two or more simple forms, as the cube and octahedron (*figs.* 156, 157), to be constructed round a common centre, and of such

*Fig.* 156.*Fig.* 157.

dimensions, that certain parts of each simple form shall project beyond the limits of the other, then the combination (represented by the shaded portion of the figures) occupies that portion of space which is common to both the simple forms; those portions of each being excluded, which project beyond the space enclosed by the other.

In any combination of simple forms, the one whose faces are most developed, and consequently determine the general aspect of the crystal is called the dominant form; thus in the combination above represented, the dominant form in *fig.* 156 is the octahedron and in *fig.* 157 the cube. The other (subordinate or secondary) faces are described according to the manner in which they are related to the dominant faces.

The secondary faces of a crystal may replace either the edges or the angles of the dominant form. If an edge is replaced by a face which makes equal angles with the two contiguous faces of the crystal, it is said to be symmetrically or perpendicularly truncated; if, on the other hand, the secondary face is unequally inclined to the two faces, which would form the edge of the crystal, the edge is said to be obliquely truncated. The cube in *fig.* 158 has its edges perpendicularly, that in *fig.* 159 has them obliquely truncated. If an edge of the dominant form is replaced by two similar faces, as in the cube (*fig.* 160) it is said to be bevelled. In like manner, a solid angle or summit of a crystal is said to be symmetrically or perpendicularly trun-

*Fig.* 158.*Fig.* 159.

cated when it is replaced by a face which is equally inclined to all the faces composing the solid angle; obliquely truncated when the truncating face is unequally inclined to those faces. *Fig.* 161 is an octahedron with the summits symmetrically truncated. *Fig.* 162 an oblique rhombic prism, in which the solid angle to the right above is obliquely truncated by the face  $+ P \infty$ , which is unequally inclined to the faces  $\infty P$  and  $oP$ .

The face which replaces the solid angle is said to be set (or to rest) symmetrically or perpendicularly on an edge, when it is equally inclined to the two faces forming the edge; obliquely in the contrary case; in *fig.* 162 the truncating face  $+ P \infty$  is set



Fig. 160.

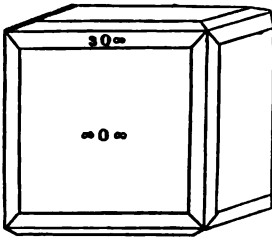
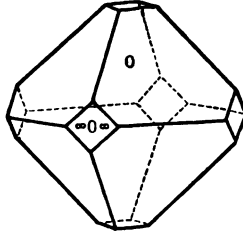
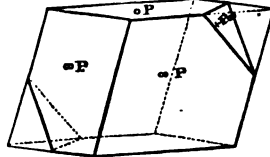


Fig. 161.



symmetrically or perpendicularly on the prismatic edge to the right, obliquely on the edge between  $oP$  and  $\infty P$  to the right in front. The face replacing the solid angle is said to be set (or to rest) symmetrically on a face of the crystal, when the plane angles which it makes with this face at the combination-edge are equal, obliquely if they are unequal; thus, in *fig. 162*, the face  $+P$  is set symmetrically on the face  $oP$ , but obliquely on the face  $\infty P$  to the right in front.

Fig. 162.



A solid angle replaced by a number of faces which together make a more obtuse solid angle, is said to be acuminated. The number of the acumination-

Fig. 163.

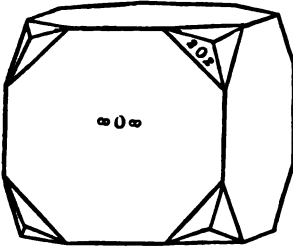
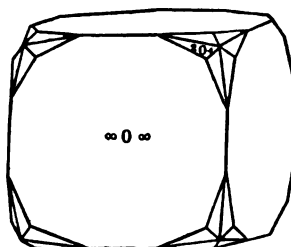


Fig. 164.



faces may be equal to, or half, or double of that of the original faces of the summit. Thus the solid angles of the cube, which are three-faced, may be acuminated with three faces, as in *fig. 163*, or with six, as in *fig. 164*. The six-faced summits of *fig. 165*, which is a form of calc-spar (i. 722), are sometimes replaced by three-faced summits, as in *fig. 166*.

Fig. 165.

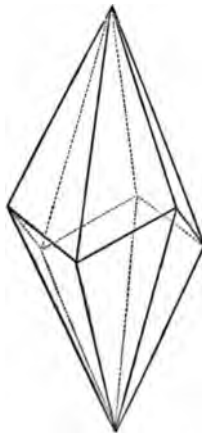
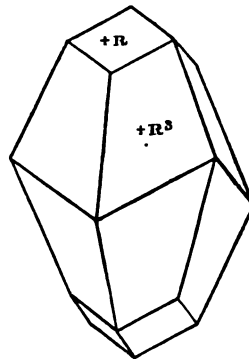


Fig. 166.



In prismatic crystals, *i.e.* such as are extended principally in one direction, the terms *beveling* and *acumination* are used to describe the conformation of the extremities. *Fig. 167* is a six-sided prism, acuminated at each end by six isosceles triangles,  $P$ , resting symmetrically on the prismatic faces. *Fig. 168* is a quadratic prism acuminated with rhombic faces,  $P$ , resting symmetrically on the prismatic edges. *Fig. 169* is a rhombic prism, whose extremities are bevelled by triangular faces  $\tilde{P} \infty$ , resting symmetrically on the acute prismatic edges.

Fig. 167.

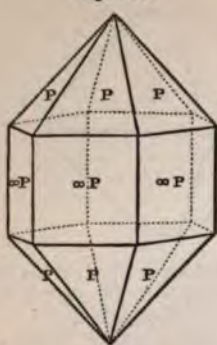


Fig. 168.

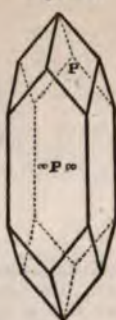
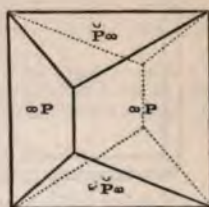


Fig. 169.



**Axes.** In all perfectly developed crystals (with a few exceptions, to be afterwards considered as cases of hemihedry), every face, edge, or summit on one side or extremity, has an equal and similar face, edge, or summit opposite to it at the other side or extremity of the crystal, and if the opposite summits, or the middle points of opposite edges or faces \* be joined by straight lines, all lines so drawn will cross one another in a single point called the centre of the crystal. Lines drawn through this point and in such directions that the faces of the crystal are symmetrically disposed with respect to them, are called *Axes*.

Similar axes are those which terminate in similar parts of the crystals; dissimilar axes, such as terminate in dissimilar parts. In the regular octahedron (*fig. 170*), in which all the summits are similar, the three axes  $xx'$ ,  $yy'$ ,  $zz'$ , joining those summits, are likewise similar. In the double six-sided pyramid (*fig. 171*), the horizontal axes which join the opposite four-faced summits are similar to each other, but dissimilar to the vertical axis.

Fig. 170.

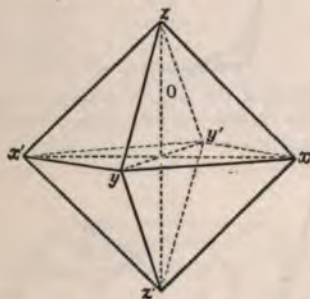
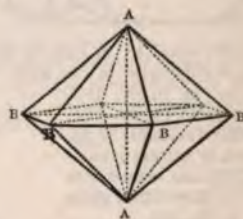


Fig. 171.



**Poly-axial and Mono-axial Forms.** Polyaxial forms are those in which no single axis can be drawn dissimilar to all the rest, *e. g.* in the cube and regular octahedron. Those forms, on the contrary, in which one or more axes can be drawn dissimilar to all the rest, are called *mono-axial*. If only one such singular axis can be drawn in the crystal, it is called the *principal axis*, the others being called *secondary*; and in describing the crystal, it is generally supposed to be placed so that the principal axis is directed from top to bottom (vertically, if it is perpendicular to the secondary axes). If two or more axes exist dissimilar to all the rest, neither can be regarded absolutely as the principal, but it is usual, for convenience, to consider one of them as such, generally the one in whose direction the crystal is most elongated. Such an axis is called a *relative principal axis*.

In mono-axial forms, the edges and summits through which the principal axis passes are called *terminal*, the others *lateral*; thus, in *fig. 171*, the summits A A, and the

\* The middle point of a plane surface is the same as its centre of gravity; thus, in a triangle, it is the point of intersection of the straight lines drawn from the angles to the centres of the opposite sides.



edges A B, &c., are terminal; the summits B and the edges B B, which join them, are lateral. In polyaxial forms this distinction does not exist.

**Mode of describing Simple Crystalline forms.** The form of a crystal is determined by the position of its faces with regard to certain axes given in position. Suppose, for example, that the crystal is symmetrical with regard to three axes crossing one another at right angles, and passing through the same point, viz. the centre of the crystal (p. 120); then the position of each face of the crystals will be given by the distance from the centre at which it meets the three axes; and as all the faces of a simple form are similar, and similarly situated with regard to the axes, the position of this one face will determine the entire form. Thus, if each face of the crystal meets the three axes at equal distances from the centre, we shall have a figure bounded by eight equal equilateral triangles, viz. the regular octahedron (*fig. 170*); and if the distances at which the faces cut the axes be called  $a$ , such a figure may be denoted by the formula,  $a : a : a$ . A face which cuts two axes at equal distances from the centre, and the third at  $n$  times that distance, will in like manner be denoted by  $a : a : n a$ . If the number  $n$  be infinite, the face in question will be parallel to one of the axes (in other words, will not intersect it at any finite distance), and the formula will become  $a : a : \infty a$ . A face parallel to two axes is denoted by  $a : \infty a : \infty a$ .

**Zones.** A number of faces of a crystal parallel to either of the axes are said to form a zone, or to lie in the same zone; thus the cube (*fig. 150*) has four faces parallel to each of the axes passing through the middle points of its sides; so likewise each axis of the regular octahedron, joining the centres of the opposite edges, has a zone of four faces parallel to it; the six prismatic faces of the ordinary form of rock-crystal (*fig. 154*), form a zone parallel to the vertical axis. The faces of a zone cut one another in edges parallel to each other, and to the axis of the zone.

**Holohedral and Hemihedral forms.** A simple form, bounded by the greatest number of similar faces that can be arranged in different directions round the common centre, is called a holohedral (fully developed) form; thus, the greatest number of faces that can meet three rectangular axes at equal distances from the point of intersection is eight, the resulting figure being the regular octahedron (*fig. 170*), which is therefore a holohedral form; but four such faces are sufficient to form a closed figure, viz. the regular tetrahedron (*fig. 190*). Such a form, enclosed by only half the number of faces that might be drawn round the centre, according to the law which determines their position, is called a hemihedral form (half-developed). Simple forms also occur, containing only one-fourth of the number of faces that might exist according to the given law of symmetry; such forms are called tetartohedral.

**Simple Crystals and Twin Crystals.** Holohedral crystals, whose faces are all symmetrically disposed about a single system of axes are called simple crystals (an expression not to be confounded with *simple form*). Crystals are, however, frequently met with, the opposite sides of which are symmetrically disposed round different systems of axes. Such crystals are called twins (also macles): they may be regarded as aggregates of two simple crystals, having their axes more or less inclined to each other.

**Crystallographic Systems.** The number of crystalline forms occurring in nature and produced by artificial processes, is so large, that some mode of classifying them is absolutely necessary. All systems of classification are founded on the symmetrical development of crystals with regard to certain axes.

The form of any solid whatever may be determined by referring it to three rectilinear axes intersecting one another in a single point: and with regard to crystals, observation shows that some are symmetrically developed about three axes intersecting one another at right angles; others, with respect to axes more or less obliquely inclined to each other: the former are called orthometric, the latter clinometric forms. Of the orthometric forms, some are equally developed in the direction of all three axes, others equally in two only, others unequally in all three. Some forms (the hexagonal) are more conveniently referred to a system of four axes. On these different modes of development are founded the following seven crystallographic systems:

I. The Monometric or Regular system, the forms of which are symmetrically disposed about three rectangular axes, all of equal length.

II. The Dimetric or Quadratic system, the forms of which are symmetric about three rectangular axes, two of equal, the third of different length.

III. The Hexagonal system, the forms of which are symmetric about four axes, three of which are of equal length, situated in the same plane, and inclined to one another at angles of  $60^\circ$ , while the fourth is of different length and at right angles to the plane of the other three.

IV. The Trimetric or Rhombic system, including the forms which are symmetric about three rectangular axes of unequal length.

V. The Monoclinic system, including the forms which are symmetric about three axes, two at right angles to each other, the third (the principal axis), perpendicular to one of them and oblique to the other.

VI. The Diclinic system, including forms which are symmetric about three axes, two of which are at right angles to each other, and the third oblique to both.

VII. The Triclinic system, including forms symmetric about three axes, all oblique to each other.

The first system comprises the polyaxial forms; the second and third, forms with absolute principal axis; the others, the mono-axial forms with relative principal axis.

Forms belonging to the same crystallographic system are related to each other by several natural affinities.

1. *It is only the simple forms of the same system that can combine into a complex form.*—For in all fully developed (holohedral) natural crystals, it is found that all the similar parts, if modified in all, are modified in an exactly similar manner (in hemihedral forms, half the similar edges and angles alternately situated are similarly modified). Now this can be the case only when the dominant form and the modifying form are developed according to the same law of symmetry. Thus, if a cube and a regular octahedron are developed round the same system of axes (as in *figs. 156, 157*), each summit of the cube is cut off to the same extent by a face of the octahedron, or *vice versa*. But a cube could never combine in this manner with a rhombic octahedron, because it would be impossible to place the two forms in such a manner that similar parts of the one should throughout replace similar parts of the other.

2. *Crystals belonging to the same system are intimately related in their optical properties.*—Crystals belonging to the regular system (as the diamond, alum, rock-salt, &c.), refract light in the same manner as amorphous bodies; that is to say, they have but one refractive index, and a ray of light passing through them in any direction is refracted singly. But all other crystals refract doubly, that is to say, a ray of light passing through them (except in certain directions) is split into two rays, the one called the *ordinary* ray, being refracted as it would be by an amorphous body, the other, called the *extraordinary* ray, being refracted according to peculiar and more complex laws (see *LIGHT*). Now the crystals of the dimetric and hexagonal systems (those with an absolute principal axis) resemble each other in this respect, that in all of them there is *one* direction, called the optic axis, or axis of double refraction (coinciding with the principal crystallographic axis), along which a ray of light is refracted singly, while in all other directions it is refracted doubly; whereas in crystals belonging to the other systems, viz. the trimetric and the three clinometric systems, there are always *two* directions or axes, along which a ray is singly refracted.

3. *Crystals belonging to the same system resemble each other in their mode of conducting heat.*—Amorphous bodies and crystals of the regular system conduct heat equally in all directions, so that, supposing a centre of heat to exist within such a body, the isothermal surfaces will be spheres. But crystals of the dimetric and hexagonal systems conduct equally, only in directions perpendicular to the principal axis, so that in such crystals the isothermal surfaces are ellipsoids of revolution round that axis; and crystals belonging to either of the four other systems conduct unequally in all directions, so that in them the isothermal surfaces are ellipsoids with three unequal axes. (See *HEAT*.)

### Monometric or Regular System.

*Tessular, Isometric, or Cubic System.*—All forms of this system are similarly and equally developed in three directions at right angles to each other; in other words, they are symmetrical about three rectangular axes meeting in a common centre. The position of each face is determined by the distances from the centre at which it meets the three axes (p. 121.) the following being all the cases that can occur:—

- A. 1. Each face (extended if necessary) meets all three axes at equal distances from the centre: the formula of such a face is  $a : a : a$ .
- B. 2. Each face meets two of the axes at equal distances from the centre, and the third at a different distance:
3. Each face meets two of the axes at an infinite distance from the centre (*i. e.* it is parallel to these two axes), and the third at a finite distance. Formula  $a : \infty : \infty$ .
3. Or two axes at equal and finite distances, the third at an infinite distance,  $a : a : \infty$ .
4. Or two axes at equal and finite distances from the centre, the third also at a finite but less distance. Formula  $a : ma : ma$  [ $m > 1$ ].
5. Or two axes at equal and finite distances, the third at a greater distance. Formula  $a : a : ma$  [ $m > 1$ ].
- C. Each face cuts the three axes at different distances from the centre:



6. Two axes at finite, the third at an infinite distance,  $a : m a : \infty a$ .
7. All three at finite distances,  $a : m a : n a$ .

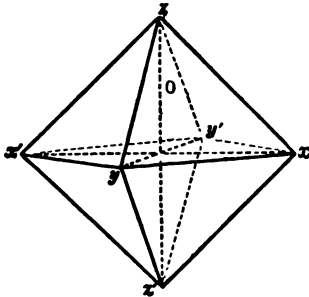
We now proceed to determine the forms given by these several conditions.

1. The form in which each face meets all the three axes,  $xx, yy, zz$ , at equal distances,  $a$ , from the centre is evidently bounded by eight equilateral triangles. This form is the regular octahedron (*fig. 172*). It has twelve equal edges, in which the faces meet each other at angles of  $109^{\circ} 28'$ , and six equal four-faced solid angles or summits, through which the axes pass. A summit thus situated, in any form of the regular system, is called an octahedral summit; where such summits occur, they are always six in number.

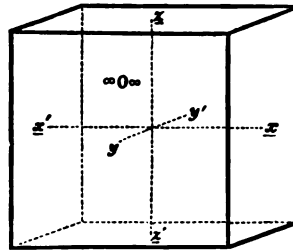
The crystallographic formula of the regular octahedron is  $a : a : a$ , usually abbreviated into the symbol  $O$ .

The regular octahedron is the form of many crystals, both natural and artificial; *e.g.* red copper ore, magnetic iron ore, alum, chrom-alum, sal-ammoniac crystallised from its aqueous solution, chloride of sodium from a solution containing urea, &c.

*Fig. 172.*



*Fig. 173.*

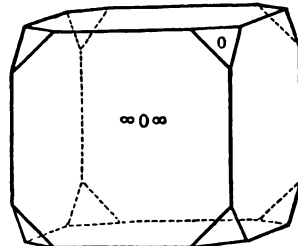


2. The simple form  $a : \infty a : \infty a$ , or  $\infty O \infty$ , in which each face meets one axis at the finite distance  $a$ , and is parallel to the other two, is evidently the cube or hexahedron (*fig. 173*), bounded by six equal faces, intersecting one another at right angles, and each having the form of a square. It has twelve equal edges meeting one another at right angles, and eight three-faced, equal-edged, solid angles or summits, situated in each octant at equal distances from the three axes. Summits so situated are called hexahedral or cubic; in holohedral crystals they are always present to the number of eight, if at all.

Cubic forms are frequently exhibited by bismuth, chloride of sodium, iodide and chloride of potassium, sal-ammoniac crystallised from a solution containing urea; also by fluor-spar, galena, and other minerals.

The cube and octahedron are often found combined together; the one or the other form predominating, according to the relative length of their axes (*figs. 156, 157, p. 220*). If the axes of the cube are less than half as long as those of the octahedron, the combination is a modified cube, like that in *fig. 174*. If, on the contrary, the axes of the cube are more than half as long as those of the octahedron, the combination is a modified octahedron (*fig. 175*). If the axes of the cube are exactly half as long as those of the octahedron, the faces of the two forms meet only in points, and the combination is that shown in *fig. 176*, called the middle crystal. It has twelve summits, each of which is situated in the plane between two of the axes, and at equal distances from them. All summits thus situated in forms of the regular system are said to be situated, "like the summits of the middle crystal."

*Fig. 174.*



3. The formula  $a : a : \infty a$ , or  $\infty O$ , represents a solid, each of whose faces meets two of the axes at equal distances,  $a$ , from the centre, and is parallel to the third; it must therefore have twelve faces, four parallel to each axis. To define its form more particularly, draw the system of rectangular axes  $xx', yy', zz'$ , meeting in  $C$  (*fig. 77*), and set off on them the points  $x, x', y, y', z, z'$ , all at equal distances from  $C$ . Now the face passing through  $xy$ , and parallel to  $xx'$ , will intersect the face passing through  $x'y'$ , and parallel to  $xx'$ , in the line  $af$ , also parallel to  $xx'$ . Similarly the faces

Fig. 175.



Fig. 176.



parallel to  $yy'$ , and passing respectively through  $zx$ ,  $z'x'$ , will intersect in  $df$  parallel to  $yy'$ , and the lines  $zf$ ,  $z'f'$ , in which these pairs of faces intersect, form two edges of the crystal. Extending this construction all round the axes, we find that the four faces meeting in  $z$ , and the four meeting in  $z'$ , would, if extended till they intersect, form a double four-sided pyramid, represented in *fig. 177* and by the dotted lines in *fig. 178*. But there are still the faces parallel to  $zx$  to be drawn. One of these faces passes through the line  $xy$ , and its position may be determined by drawing through the middle point of  $xy$  (*fig. 178*), a line  $ik$ , parallel to  $zx$ , which will cut the edge  $zf$  of the pyramid in its middle point  $l$ ; and by joining this point with the points  $x, y$ ,

Fig. 177.

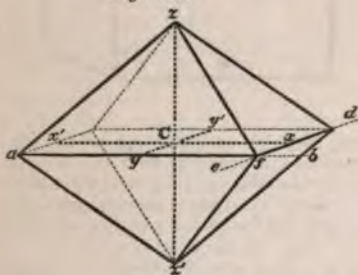
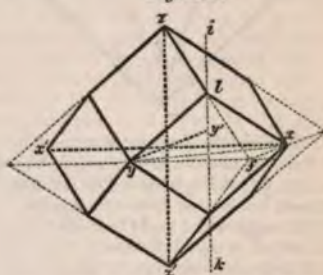


Fig. 178.



we obtain two edges of the required form,  $lx, ly$ . A similar construction carried out in the other parts of the figure finally gives the rhombic dodecahedron (also called granatohedron). It has twelve rhombic faces, with plane angles of  $109^\circ 28'$  and  $70^\circ 32'$ , and diagonals in the ratio of  $1 : \sqrt{2}$ . The edges are all equal. The summits are fourteen in number, six 4-faced, octahedral summits, A (*fig. 151*), formed by the meeting of the acute angles of the rhombuses, and eight 3-faced cubic summits, B, formed by the meeting of the obtuse edges of the rhombuses. The dihedral angles formed by the meeting of the faces are all equal to  $120^\circ$ .

The dodecahedron sometimes occurs alone in artificial crystals, more frequently in combination; in minerals it is more common as a simple form, as in garnet.

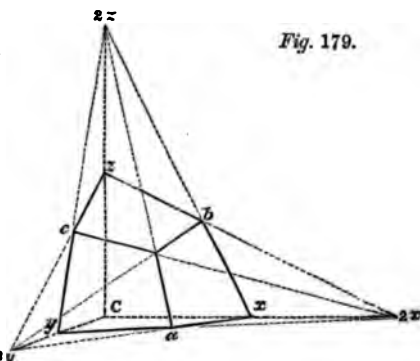
The three forms above described, the regular octahedron, cube, and rhombic dodecahedron are unique in their kind; that is to say, all individuals of each species must be exactly similar to each other; there can be no variation either in the plane angles or in the inclination of the faces. This, indeed, is sufficiently evident from the formulæ, which admit of no variation, and from the mode of construction. But in the remaining four forms of the regular system, the formulæ of which contain numerical coefficients admitting of variations in magnitude, this constancy of shape no longer exists; and accordingly we shall find that the angles vary with the magnitude of the coefficients in the formula.

4. The formula  $a : ma : ma$ , or  $m O m$ , represents a solid, each of whose faces meets one axis at the distance  $a$  from the centre, and the other two at the greater distance  $ma$ . Draw a system of rectangular axes (*fig. 179*), and, taking for example  $m = 2$ , mark off single and double distances,  $x, 2x$ , &c., on each of the three axes. It is then easy to see that the position of one face will be determined by a plane passing through the points  $y, 2x, 2x$ ; a second through  $y, 2x, 2x'$ ; a third through  $y, 2x', 2x'$ ; and a

\* The points  $x', y', z'$ , &c. (not shown in the figure) are supposed to be on the prolongations of the lines  $xC, yC, zC$ , as in the preceding figure.

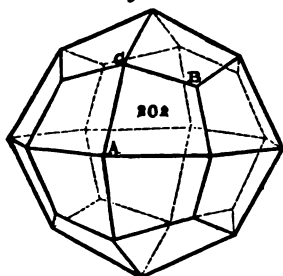


fourth through  $y$ ,  $2x'$ ,  $2x$ ; that is to say, there will be four faces meeting at the point  $y$ , and in like manner there will be four faces meeting in each of the points  $x$ ,  $x'$ ,  $y$ ,  $z$ ,  $z'$ , or 24 in all, three in each octant. Further, the face  $y$ ,  $2x$ ,  $2x'$  will meet the face  $y$ ,  $2x$ ,  $2x'$  in the line  $y$ ,  $2x$ , and the face  $z$ ,  $2y$ ,  $2x$  will meet the face  $z$ ,  $2y$ ,  $2x'$  in the line  $z$ ,  $2y$ , meeting  $y$ ,  $2x$  in the point  $c$ . Thus the edges,  $cy$ ,  $cz$ , situated in the plane  $yz$ , are determined; and a similar construction gives the edges  $ax$ ,  $ay$ , and  $bx$ ,  $bs$ . Next, to find the intersections of the three faces included within the octant  $xyz$ . The face  $z$ ,  $2x$ ,  $2y$ , intersects  $y$ ,  $2x$ ,  $2x'$  in the line  $c$ ,  $2x$ , joining  $2x$  with the intersection of  $z$ ,  $2y$ , and  $y$ ,  $2x$ ; the face  $x$ ,  $2y$ ,  $2x$ , meets  $y$ ,  $2x$ ,  $2x'$  in the line drawn from  $2x$  to  $a$ , the intersection of  $x$ ,  $2y$ , and  $y$ ,  $2x$ ; and  $x$ ,  $2y$ ,  $2x$  meets  $x$ ,  $2x$ ,  $2y$  in the line drawn from  $2y$  to  $b$ , the intersection of  $x$ ,  $2x$ , and  $z$ ,  $2x$ . This construction gives the intersections shown by the dark lines in the figure, and determines the form and position of the three faces in the octant  $xyz$ ; and the same construction repeated in the other octants gives the form shown in *figs.* 180, 181, which is called the *ikosi-tetra-*

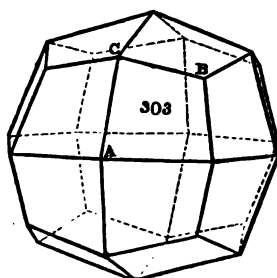


*Fig.* 179.

*Fig.* 180.



*Fig.* 181.



hedron (also leucitohedron and trapezohedron). It is bounded by 24 deltoids (quadrilaterals having two unequal pairs of equal sides), and has 26 summits, which are of three kinds; viz. six 4-faced, equal-edged, octahedral summits, A; eight 3-faced, equal-edged, cubic summits, B; and twelve 4-faced symmetric summits, C, situated like the summits of the middle-crystal (p. 123). It has also 48 edges, which are of two kinds, viz. 24 longer, A C, joining the octahedral with the symmetric summits, and 24 shorter, B C, joining the cubic with the symmetric summits.

The ikosi-tetrahedron is the intermediate form between the octahedron and the cube; for  $m = 1$ , it coincides with the octahedron; for  $m = \infty$ , with the cube. The nearer  $m$  is to 1, the more do the three faces in each octant fall into one plane, and the more nearly  $m = \infty$ , the more do the four faces round each octahedral summit, A, fall into one plane, the limit giving a cube. The inclination of the faces to one another in the longer and shorter edges is:—

	A C	B C
In 2 O 2	131° 43'	146° 27'
„ 3 O 3	144 54	129 31

The form 2 O 2 is found alone in leucite, analcime, and other minerals; 3 O 3 rarely, in native gold, silver, &c. In artificial crystals, the form 2 O 2 occurs combined in chrome-alum and common alum, when a crystal is immersed in a saturated solution mixed with a little hydrochloric acid slightly heated, so that the edges may be dissolved off, and then left to cool.

5. Formula  $a : a : ma$ , or  $m O$ , each face meeting two axes at the distance  $a$  from the centre, and the third at a greater distance,  $ma$ ;  $m$  being either a whole number or a fraction greater than 1. This form, like the preceding, has 24 faces, 3 in each octant. A construction similar to the preceding, and sufficiently indicated by the full and

Fig. 182.

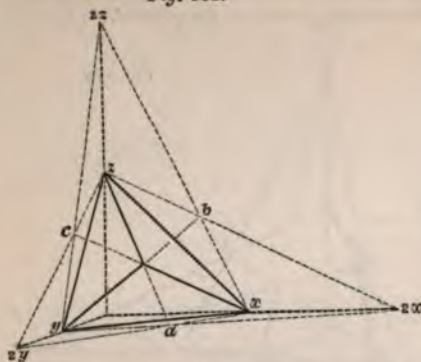
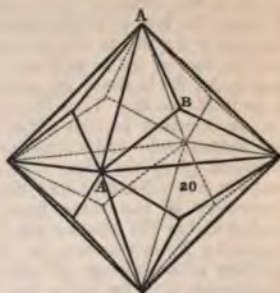


Fig. 183.



dotted lines in *fig. 182*, shows that the solid is bounded by 24 isosceles triangular faces, and has the appearance of an octahedron with triangular pyramids erected on its faces. This form is called the triakis-octahedron (also pyramidal octahedron, galenoid). *Fig. 183* shows the form 20.

The triakis-octahedron has 14 summits, six of which, A, are 8-faced, symmetric, and octahedral, and eight 3-faced, equal edged, and cubic, B. The edges are also of two kinds; 12 A A, joining the octahedral summits and forming the bases of the isosceles triangles; and 24 A B, joining the octahedral and cubic summits, and forming the equal sides of the triangles.

The triakis-octahedron,  $a : a : ma$ , is the intermediate form between the octahedron,  $a : a : a$ , and the rhombic dodecahedron,  $a : a : \infty a$ .

The plane and dihedral angles vary with the value of  $m$ , as in the following examples:—

	$\frac{3}{2}O$	2O
Plane angles at vertex of isosceles triangles . . . . .	$119^{\circ} 14'$	$118^{\circ} 4'$
Plane angles at base of triangles . . . . .	$30 \ 23$	$30 \ 58$
Dihedral angles A A . . . . .	$129 \ 31$	$162 \ 39$
Dihedral angles A B . . . . .	$141 \ 3$	$152 \ 44$

6. Formula  $a : ma : \infty a$ , or  $mO \infty$ , each face meeting two of the axes at unequal distances and being parallel to the third. To determine the number of faces in this form, mark off, on the system of rectangular axes (*fig. 184*, supposing  $m=2$ ) single and double distances on each of the axes measured from C. Then there will be four faces passing through the point 1  $y$ , two parallel to  $xz$ , through the points 2  $z$  and 2  $z'$ , and two parallel to  $yz$ , through the points 2  $x$ , 2  $x'$ ; and since the crystal is equally developed in the direction of all the three axes, there must be four similar faces meeting in

Fig. 184.

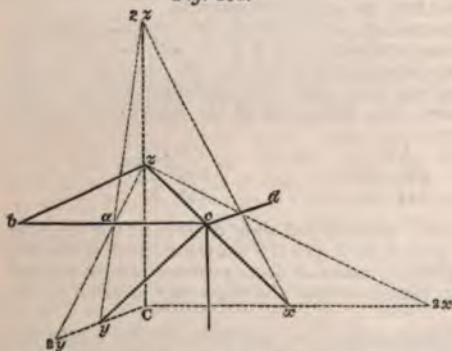
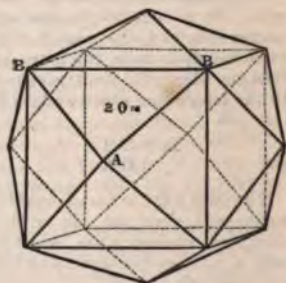


Fig. 185.



each of the points  $y'$ ,  $x'$ ,  $z'$ , that is to say, twenty-four faces in all; and by constructing each octant in the same manner as for the preceding formulae, the form is



found to be a solid (*fig. 185*), bounded by 24 isosceles triangles, having 14 summits, viz. four 4-faced equal-edged octahedral summits, A, and eight 6-faced symmetric, cubic summits B. It has 36 edges, 12 longer, B B, uniting the cubic summits, and 24 shorter, A B, joining the octahedral with the cubic summits. This figure is the *tetrakis-hexahedron*. It is intermediate between the dodecahedron  $a : a : \infty a$ , and the cube  $a : \infty a : \infty a$ . In the more commonly occurring varieties, the plane and dihedral angles are:

	20 $\infty$	30 $\infty$
Plane angle, A, at vertex of isosceles triangles	83° 38'	86° 59'
Plane angles, B, at base of triangles	48 11	46 30
Dihedral angles, A B	143 8	154 9
Dihedral angles, B B	143 8	126 52

The form 20 $\infty$  occurs uncombined in native gold and silver; 30 $\infty$  in fluor-spar. In artificial crystals these forms occur but seldom, and then only subordinate to others, as for example in sulphantimonate of sodium (Schlippe's salt), and in rock-salt which has been exposed to moist air. Faces having the disposition of this form, but in only half the full number, are of more frequent occurrence.

7. Formula  $a : ma : na$ , or  $mOn$ . Each face meets the three axes at unequal but finite distances. Such a form must have 48 faces; for through each axial extremity 2 faces can be drawn in each of the four contiguous octants, *e. g.* from  $z$  above, one face passing through the point  $ma$  or  $x$  to the right, and  $na$  or  $y$  in front, and another through  $na$  or  $x$  to the right, and  $ma$  or  $y$  in front; therefore,  $4 \times 2 = 8$  through each axial extremity, and  $6 \times 8 = 48$  in all.

To determine the form of these faces, draw the system of axes as before, and taking as an example the form  $1 : \frac{2}{3} : 3$ , or  $\frac{2}{3}O3$ , mark off on each axis (*fig. 186*), both ways, the distances 1,  $\frac{2}{3}$ , and 3. The face  $z : \frac{2}{3}y : 3x$ , forms with the face  $x : \frac{2}{3}y : 3x$  (not drawn in the figure), an edge in the direction  $z, \frac{2}{3}y$ . The same face  $z, \frac{2}{3}y : 3x$  intersects the face  $x, 3y, \frac{2}{3}x$  in the direction  $xa$ , drawn through  $x$  and the intersection of the lines  $\frac{2}{3}y, 3x$ , and  $3y, \frac{2}{3}x$ ; and lastly, it intersects the face  $y, \frac{2}{3}x, 3x$ , in the direction  $b, 3x$ , where  $b$  is the point of intersection of the lines  $x, \frac{2}{3}y$ , and  $y, \frac{2}{3}x$ . The face thus determined is a triangle, and in like manner the position of the five other faces in the octant,  $x y z$ , may be determined. The result extended symmetrically to all the other octants, is the

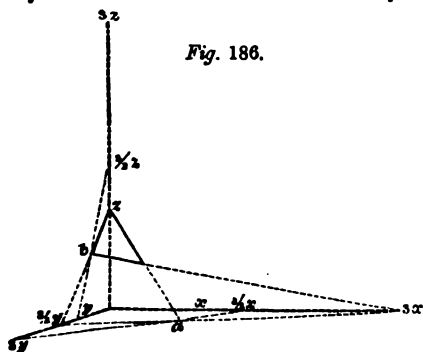


Fig. 186.

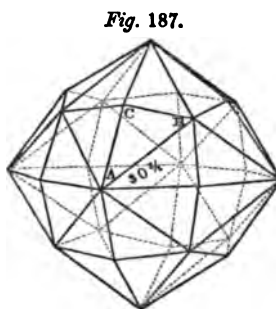


Fig. 187.

form represented in *fig. 187*, bounded by 48 scalene triangles. This figure is called the *Hexakisioctahedron* (also *tetrakonta-octahedron*, *adamantoid*, &c.). It has 26 summits of three kinds, viz. eight 6-faced symmetrical octahedral summits A, through which the axes pass; six 8-faced, cubic summits B; and twelve 4-faced symmetric summits C, situated like those of the middle crystal (p. 123). Its edges are 72 in number, and likewise of three kinds, viz. 24 edges A C, uniting the octahedral with the four-faced summits; 24 edges B C, uniting the cubic with the four-faced summits, and 24 edges A B, uniting the octahedral with the cubic summits.

The plane and dihedral angles of the figure vary with the magnitudes of  $m$  and  $n$ : for the most commonly occurring forms they are as follows:

	30 $\frac{2}{3}$	204
Plane angles A of the scalene triangles	36° 49'	39° 48'
" B	56 15	54 22
" C	86 56	85 50
Dihedral angles A C	149 0	154 47
" B C	158 13	144 3
" A B	158 13	162 15

The form 204 often occurs very predominant in crystals of fluor-spar;  $30\frac{1}{2}$  in garnet. Diamonds are also found having the form of the hexakis-octahedron, but with curved faces, so that the angles cannot be accurately measured. This form occurs but very rarely in artificial crystals: it has, however, been observed, though very subordinate, in alum crystallised from a solution containing hydrochloric acid.

**Hemihedral Forms of the Regular System.**— Suppose four alternate faces of the octahedron (*fig. 188*), viz. the right front above, left front below, left back above, and right back below, to extend so as partially to obliterate the four remaining faces; a form will be produced like figure 189; and if the extension be continued till the alternate faces completely disappear, the four-sided pyramid (*fig. 190*) will be produced, called the regular tetrahedron, and denoted by the symbol  $\frac{O}{2}$ .

Fig. 188.

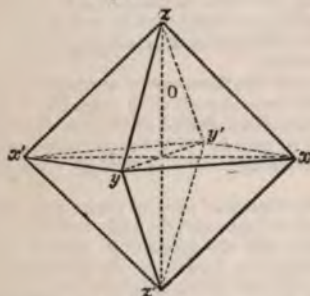


Fig. 189.



It is bounded by four equilateral triangles, has 4 three-faced summits, and 6 similar edges in which the faces are inclined at angles of  $70^\circ 32'$ . The axes pass through the middle points of each pair of opposite edges.

Fig. 190.

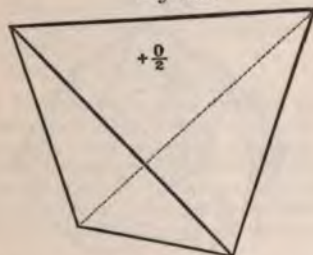
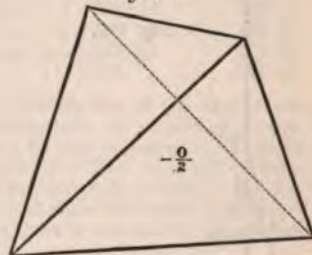


Fig. 191.



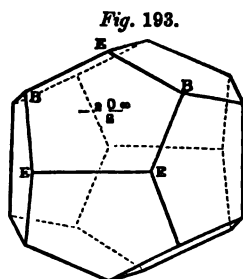
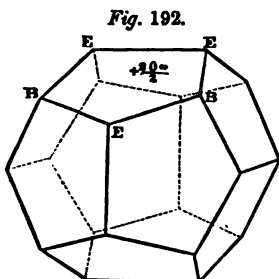
If the other four sides of the octahedron increase instead of those above-mentioned, the result will be the tetrahedron shown in figure 191, exactly similar to the former but oppositely situated. When both these tetrahedrons occur together in the same crystal, as in *fig. 189*, one of them is distinguished as  $+\frac{O}{2}$  the other as  $-\frac{O}{2}$ ; when either occurs alone the sign + or - may be omitted.

Tetrahedral faces occur in Schlippe's salt, chlorate of sodium, fahl-ore, blende, &c.

The cube and rhombic dodecahedron have no corresponding hemihedral forms. The icosi-tetrahedron, triakis-octahedron, tetrakis-hexahedron, and hexakis-octahedron all produce hemihedral forms by the growth of their alternate faces; but the only one of these forms that it is important to notice is the pentagonal dodecahedron (*fig. 192*) produced from the tetrakis-hexahedron (*fig. 185*, p. 126). This holohedral form may be regarded as a cube on each of whose six faces is erected a four-sided pyramid. Suppose now that on the top and bottom pyramids, the front and back faces grow, while the right and left disappear; that on the front and back pyramids, the right and left faces grow, while the upper and lower faces disappear; and that on the right and left pyramids, the upper and lower faces grow, while the right and left disappear; the result will be a dodecahedron whose general symbol is  $\frac{mO\infty}{2}$ . *Fig. 192* represents  $\frac{2O\infty}{2}$ .

If the other alternate faces of the holohedral form be supposed to increase, an exactly



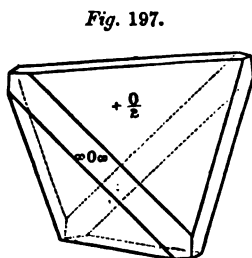
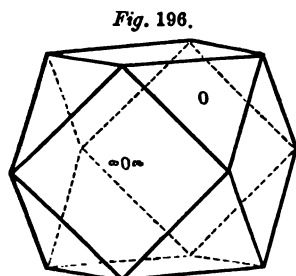
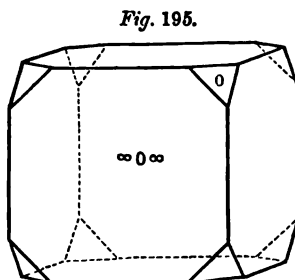
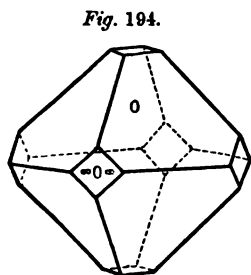


similar dodecahedron (*fig.* 193) will be formed, but differently situated; these two forms may be distinguished by the symbols  $+\frac{20\infty}{2}$  and  $-\frac{20\infty}{2}$ .

The pentagonal dodecahedron is bounded by 12 symmetric pentagons, each having four of its sides of equal length, and the fifth (the base) of different length. It has 30 edges, 6 of which, E E, are formed by the meeting of the faces at their bases, and 24, B E, forming the equal sides of the pentagons. The summits are 20 in number, 12 of which, E, formed by the meeting of a basal edge E E, and two equal edges B E, are situated in the planes of the axes, but at different distances therefrom, and 8 others, B, formed by the meeting of three equal edges of the pentagons and situated like the summits of the cube. The axes pass through the middle points of each pair of opposite basal edges.

The pentagonal dodecahedron has not yet been observed in its complete form in artificial crystals; among minerals it is especially exhibited by iron-pyrites and cobalt-glance.

**Combinations of the Simple Forms of the Monometric system.** These combinations are very numerous; we shall here notice some of the most important. In expressing a combination symbolically, the symbol of the dominant form is usually written first:



1. *Cube and Octahedron:*

$O. \infty O \infty$  (*fig.* 194). Alum, chlorstannate of ammonium, cobalt-pyrites.

$\infty O \infty . O$  (*fig.* 196). Chloride of zinc, galena.

$O$  and  $\infty O \infty$  equally developed (*fig.* 196), forming the "middle crystal" (p. 123). Nitrate of lead.

Fig. 198.

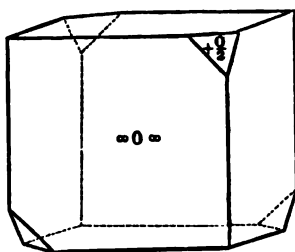


Fig. 199.

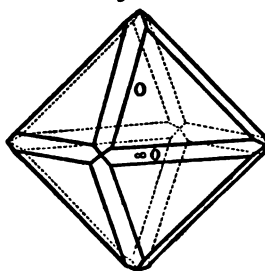


Fig. 200.

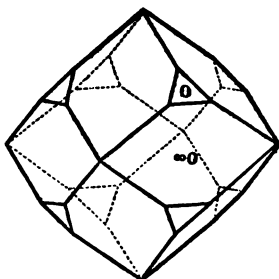


Fig. 201.

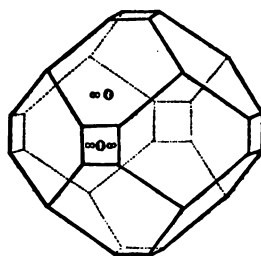


Fig. 202.

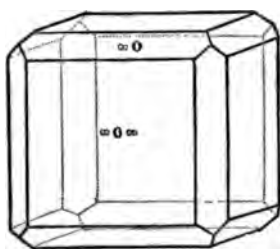
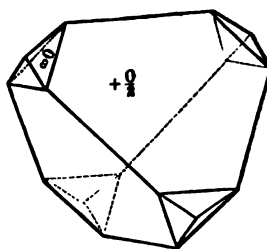


Fig. 203.



1a. *Cube and Tetrahedron:*

$\frac{O}{2} \cdot \infty O \infty$  (fig. 197). Boracite.

$\infty O \infty \cdot \frac{O}{2}$  (fig. 198). Boracite, Cube-ore.

2. *Dodecahedron and Octahedron:*

$O \cdot \infty O$  (fig. 199). Alum and red copper-ore.

$\infty O \cdot O$  (fig. 200). Magnetic iron-ore.

2a. *Dodecahedron and Tetrahedron:*

$\frac{O}{2} \cdot \infty O$  (fig. 203). Sodio-uranic acetate. Fahl-ore.

3. *Dodecahedron and Cube:*

$\infty O \cdot \infty O \infty$  (fig. 201). Garnet (rarely).

$\infty O \infty \cdot \infty O$  (fig. 202). Alum, crystallised from solution containing free alkali; chloride of potassium from solution containing mercuric chloride, frequently; fluor-spar rarely.



Fig. 204.

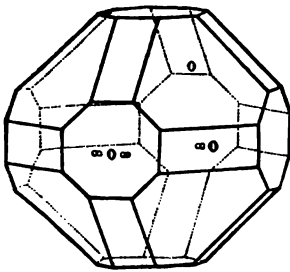


Fig. 205.

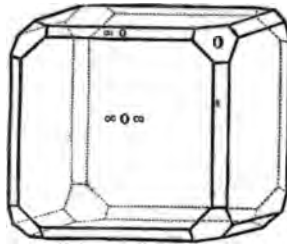


Fig. 206.

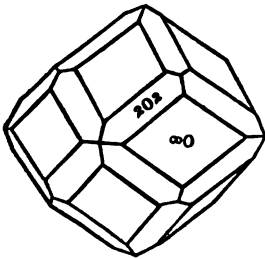


Fig. 207.

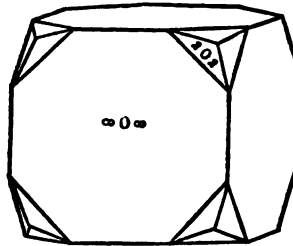


Fig. 208.

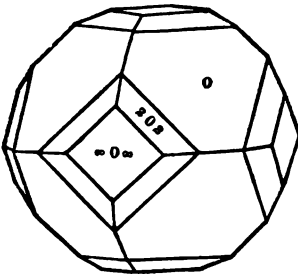
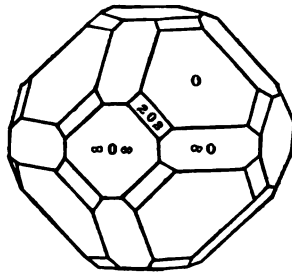


Fig. 209.



4. *Dodecahedron, Cube and Octahedron:*

$0 \cdot \infty 0 \infty \cdot \infty 0$  (fig. 204), in which, however, the  $0$ -faces do not predominate very much; occurs commonly in alum.

$\infty 0 \infty \cdot 0 \cdot \infty 0$  (fig. 205); frequently in alum from solution containing free alkali; also in chloride of sodium from solution containing chloride of bismuth.

4a. *Dodecahedron, Cube and Tetrahedron:*

These combinations, which occur in Boracite, are similar to those of the dodecahedron, cube, and octahedron, excepting that only four octahedral faces are present instead of eight.

5. *Combinations of Icosi-tetrahedron:*

$\infty 0 \cdot 202$  (fig. 206). Melanite.

$\infty 0 \infty \cdot 202$  (fig. 207). Analcime.

$0 \cdot \infty 0 \infty \cdot 202$  (fig. 208). Alum and chrome-alum (rarely).

$0 \cdot \infty 0 \infty \cdot \infty 0 \cdot 202$  (fig. 209). Alum.

Fig. 210.

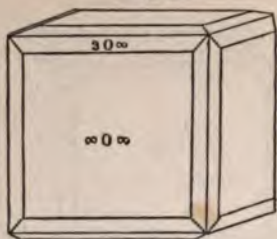


Fig. 211.

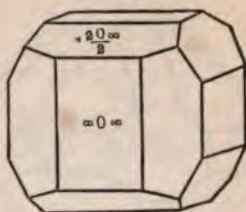


Fig. 212.

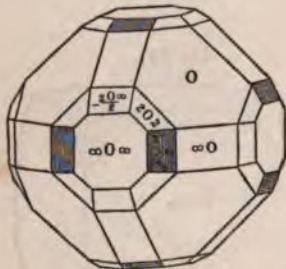
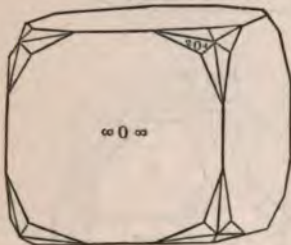


Fig. 213.



Fig. 214.



#### 6. Combinations of the Tetrakis-hexahedron:

$\infty 0 \infty . 30 \infty$  (fig. 210). Fluor-spar. A similar combination,  $\infty 0 \infty . 20 \infty$ , is produced when cubes of rock-salt are exposed to moist air.

$\infty 0 \infty . + \frac{20 \infty}{2}$  (fig. 211). Iron pyrites. Cobaltine.

$0 . \infty 0 \infty . \infty 0 . 202 . + \frac{20 \infty}{2} . - \frac{20 \infty}{2}$  (fig. 212). Alum.

#### 7. Combinations of the Hexakis-octahedron:

$0 . 30 \frac{3}{2}$  (fig. 213). Alum (apparently).

$\infty 0 \infty . 204$  (fig. 214). Fluor-spar.

### Dimetric or Quadratic System.

*Square Prismatic, Pyramidal, Tetragonal, Monodimetric System (Zwei- und einaxiges, viergliedriges System).*

Crystals belonging to this system are symmetric about three rectangular axes, two of equal, the third of different length; and may, therefore, be so placed as to appear equally developed in two horizontal directions at right angles to each other (right and left, and backwards and forwards), but differently in the vertical direction. The vertical or principal axis (p. 120) will be denoted by  $c$ , the horizontal or secondary axes by  $a$ . All sections perpendicular to the principal axis are squares or figures derived therefrom.

In this, as in the monometric system, the most general form is one, each of whose faces (produced if necessary) meets the three axes at different distances from the centre. Let these distances be  $a$  and  $na$  for the secondary axes ( $n$  being a multiplier either greater or less than unity), and  $c$  for the principal axis. To determine the form, draw two rectangular axes (fig. 215), and supposing, for example,  $n = \frac{3}{2}$ , set off from the centre the distances  $a$  and  $\frac{3}{2}a$ , and join each point  $a$  on the one axis with  $\frac{3}{2}a$  on the other, as shown by the dotted lines in the left upper quadrant. The portions of these lines contained between the several points  $a$  and the intersections of these dotted lines will form an equilateral octagon; and if from each of the angles of this



Fig. 215.

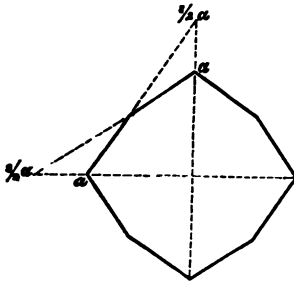
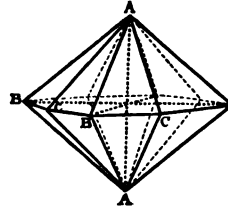


Fig. 216.



octagon straight lines be drawn to the extremities  $c$  of the principal axis (perpendicular to the plane of the paper), the planes passing through these lines will enclose a double eight-sided pyramid (fig. 216), bounded by sixteen scalene triangles,  $ABC$ , the summits  $B$  being situated at the ends of the horizontal axes, and the summits  $C$  at angular distances of  $45^\circ$  therefrom. This figure evidently fulfils the condition essential to the forms of the dimetric system, of being equally developed in the direction of two rectangular axes, but differently in the direction of the third. It may be represented by the formula :

$$a : na : c.$$

The inclinations of the edges  $BC$  to each other (or the angles of the octagon, fig. 215), vary with the value of  $n$ . The more  $n$  approaches to unity, the more nearly do the points  $na$  (fig. 216) approach to  $a$ , and the more nearly do the lines joining these points ( $BC$ ,  $CB$  in fig. 216) approach to coincidence, the angles  $C$  of the base becoming greater; and when  $n=1$ , or the formula becomes  $a : a : c$ ; the angles  $C$  become  $= 180^\circ$ ; in other words, the lines  $BC$ ,  $CB$  coincide; the octagon becomes a square; and the double eight-sided pyramid is reduced to a double four-sided pyramid with a square base (fig. 217), having its angles  $B$  situated at the extremities of the horizontal axes.

Fig. 217.

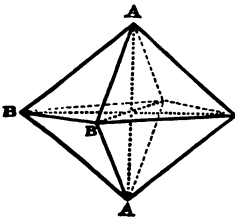
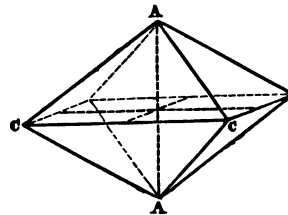


Fig. 218.



If, on the other hand,  $n$  increases, the angles  $C$  (fig. 216) become less, and the angles  $B$  more and more obtuse; and finally, when  $n = \infty$ , or the formula becomes  $a : \infty a : c$ , the angles  $B$  become  $= 180^\circ$ , or the two horizontal lines  $BC$ ,  $CB$ , drawn from the extremities of each axis, merge into single straight lines parallel to the other axis; and the base of the pyramid becomes a square, having the middle points of its sides at the extremities of the secondary axes, and its angles  $C$  equidistant from those points, as in fig. 218.

The symbols of the three forms just described are abbreviated as follows: —

$$\begin{aligned} a : a : c \text{ (fig. 217)} &= P \\ a : na : c \text{ (fig. 216)} &= Pn \\ a : \infty a : c \text{ (fig. 218)} &= P\infty. \end{aligned}$$

It appears then that a square pyramid may be represented by the formula  $a : a : c = P$ , or  $a : \infty a : c = P\infty$  (the ratio  $c : a$  being however different in the two cases), according as the secondary axes pass through the angles or the middle points of the sides of the base. When two pyramids so related to each other occur together in the same crystal,  $P$  is regarded as the primary form, and is called the square pyramid of the first order;  $P\infty$  the pyramid of the second order.

A square pyramid is more or less acute, according to the ratio between the principal and secondary axes. When  $a$  is very nearly equal to  $c$ , the pyramid is scarcely distinguishable in outward form from the regular octahedron (*fig. 149*); the two forms may, however, always be distinguished by their modifications, the edges and summits of the regular octahedron being all modified alike, whereas in a square pyramid the terminal edges  $AB$  (*fig. 216*) may be modified differently from the lateral edges  $BB$ , and the summits  $AA$  at the ends of the principal axis differently from the summits  $B$  at the ends of the secondary axes.

As the ratio of  $c$  to  $a$  becomes greater, the pyramid becomes more and more acute, and the angles of the planes meeting in the lateral edges  $BB$  (*fig. 217*),  $CC$  (*fig. 218*), or  $BC$  (*fig. 216*), approach more nearly to  $180^\circ$ ; and finally, when the ratio  $c : a$  becomes infinitely great, this angle becomes  $= 180^\circ$ , and the pyramid is reduced to a prism of indefinite length, having its sides parallel to the principal axis.

When two quadratic pyramids, in which the ratio  $c : a$  is different, occur together in the same crystal, one of them is regarded as the primary form, and denoted by one of the formulæ already given; the other in which the ratio of  $\frac{c}{a}$  is  $m$  times that in the former ( $m > 1$ ), is denoted by prefixing the symbol  $m$  to  $c$  in the full formula, or to  $P$  in the abbreviated formula; thus:—

Square pyramids of the first order . . . . .	$a : a : mc = mP$
Octagonal pyramids . . . . .	$a : na : mc = mPn$
Square pyramids of the second order . . . . .	$a : \infty a : mc = mP\infty$

When in either of these formulæ  $m$  becomes infinite, the corresponding pyramid becomes a prism, as already explained.

When  $m = 0$ , the pyramid is reduced to a plane, called the terminal face, or end-face,  $oP$ , parallel to the plane of the secondary axes.

Among pyramids of the second order occurring together with a primary form  $P$ , it is usual to distinguish particularly the two following:

*a.* The next obtuser pyramid is that whose faces have the same position and inclination with respect to the principal axis, as the terminal edges of the primary form. For the primary form  $a : a : c$ , or  $P$  (*fig. 217*); the next obtuser pyramid is evidently  $a : \infty a : c$ , or  $P\infty$  (*fig. 218*), having for its base the outer dotted square,  $bced$  (*fig. 219*), whose sides are drawn parallel to the axes, through the angles of the base of the primary form; and generally, for every square pyramid of the first order,  $mP$ , the next obtuser pyramid is  $mP\infty$ . The terminal edges of  $P$  are symmetrically truncated by the faces of  $mP\infty$ .

*b.* The next acuter pyramid is that whose terminal edges have the same position and inclination with respect to the principal axis, as the faces of the primary form. The primary form having for its base the square represented by the continuous lines in *fig. 219*, the next acuter pyramid will have the same principal axis, and the base  $ghki$ , whose angles are at the middle points of the sides of the primary form. The formula of this pyramid is  $\frac{1}{2}a : \infty a : c$ , or  $a : \infty a : 2c$ , or  $2P\infty$ ; and generally, for every square pyramid of the first order,  $mP$ , the corresponding next acuter pyramid is  $2mP\infty$ . The terminal edges of the latter are symmetrically truncated by the faces of  $mP$ .

Fig. 219.

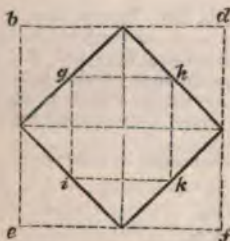


Fig. 220.



**Combinations of the Holohedral forms of the Dimetric system.** The square and octagonal pyramids and prisms above described are the only simple holohedral forms of the dimetric system. The following are some of their principal com-



binations:—When two square pyramids of the same order occur together in a crystal, the more acute of the two is acuminated in the direction of the principal axis by the faces of the more obtuse, which rest on the faces of the former, as in *fig. 220*. In sulphate of nickel, which crystallises in this manner, the ratio  $c : a = 1.888$  in the more obtuse pyramid, and  $0.944$  in the more acute pyramid, the length of  $c$  in the two pyramids referred to a secondary axis as unity, being in the ratio of  $2 : 1$ . In all such combinations, it is found that the principal axes of the two pyramids bear to one another a simple ratio, as  $3 : 1$ ,  $3 : 2$ , &c.

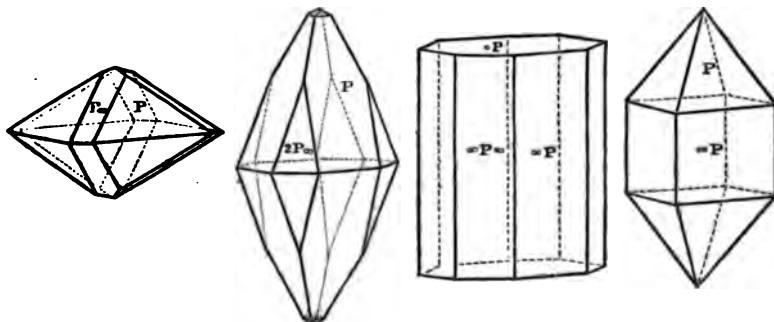
When two square pyramids of different orders occur together, the faces of the one truncate the edges or the summits of the other. *Fig. 221* represents a form of tin-stone, in which the terminal edges of the primary form  $P$  are symmetrically truncated by the faces of the next obtuser pyramid  $P\infty$ . *Fig. 222* is a form of anatase, in which the terminal summits of  $P$  are acuminated by  $\frac{1}{2}P$ , and the lateral summits are bevelled by the faces of the next acuter pyramid,  $2P\infty$ . The terminal edges of this latter pyramid may also be regarded as very broadly truncated by the faces of  $P$ .

Fig. 221.

Fig. 222.

Fig. 223.

Fig. 224.



Combinations of prisms and pyramids of the different orders, with or without the terminal face  $\infty P$ , are of frequent occurrence. *Fig. 223* represents an octagonal prism formed by the prismatic faces of the first order,  $\infty P$ , truncated by the prismatic faces of the second order,  $\infty P\infty$ , and terminated above and below by  $\infty P$ . This form is seen in acetate of copper and calcium,  $C^2H^2CuCaO^3$ .

$\infty P.P$  (*fig. 224*) is a form of potassio-uronic acetate, a square prism with pyramidal summits resting on the prismatic faces.

*Figs. 225, 226, 227* represent combinations of the forms  $P . \infty P \infty$  in various proportions.

$P . \infty P \infty$  (*fig. 225*), with  $P$  predominant, is found in mellite or honeystone.

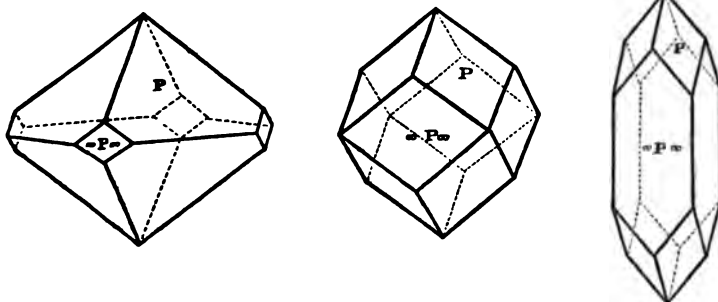
$P$  and  $\infty P \infty$  equally developed (*fig. 226*), which has very much the appearance of a rhombic dodecahedron, is exhibited by potassio-cupric chloride,  $KCl.CuCl$ .

$\infty P \infty . P$  (*fig. 227*) is a form of apophyllite.

Fig. 225.

Fig. 226.

Fig. 227.



The following figures (*figs. 228—231*) represent combinations of square pyramids with the terminal face  $\infty P$ ; they are all forms of sulphate of nickel,  $Ni^2SO^4 + 3H^2O$ . In all these combinations, it may be observed that pyramids similarly situated between the

Fig. 228.



Fig. 229.

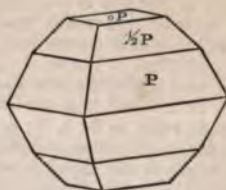
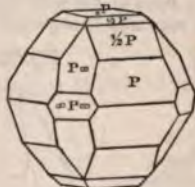


Fig. 230.



Fig. 231.

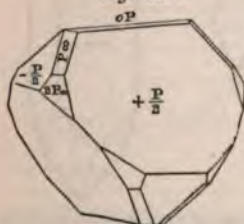


axes form combination-edges parallel to the base, *e. g.*,  $oP$ ,  $\frac{1}{2}P$ ,  $P$ , and  $P\infty$ .  $\infty P\infty$  (fig. 231), whereas pyramids and prisms differently situated with regard to the axes form combination-edges inclined to the base, *e. g.*  $P$  and  $\infty P\infty$ , in figs. 225, 226, 227, 230, 231; also  $P$  and  $P\infty$  in figs. 230, 231. This rule is of great use in determining the relations of the faces in complicated combinations.

**Hemihedral Forms.** A square pyramid may become hemihedral in the same manner as a regular octahedron (p. 128), viz. by the extension of four alternate faces till the others are obliterated. The figure thus produced, called a quadratic sphenoid, is a four-sided pyramid distinguished from the regular tetrahedron by the form of its faces, which are not equilateral but isosceles triangles. The principal axis terminates in the middle points of two of the edges (terminal edges); the secondary axes in the middle points of the four other edges (lateral edges). A quadratic sphenoid is denoted by the symbol  $\frac{mP}{2}$  or  $\frac{mP\infty}{2}$ , according to that of the pyramid from which it is formed. The signs + and - prefixed to these symbols have the same meanings as in the case of the regular tetrahedron (p. 128).

Sphenoids rarely occur alone; a solution of cyanide of mercury, however, sometimes yields by spontaneous evaporation perfectly developed sphenoids in which  $\frac{c}{a} = 0.985$ . More frequently sphenoids occur in combination, *e. g.* with their terminal edges truncated by the face  $oP$ , and their lateral edges by  $\infty P\infty$ . The summits of  $\frac{P}{2}$  may also be replaced by the faces of the opposite sphenoid, in which case they are distinguished as  $+\frac{P}{2}$  and  $-\frac{P}{2}$ . A combination of these two forms equally developed has the external form of a square pyramid, but may generally be distinguished therefrom by the different modifications of its edges and summits. Fig. 232 is a form of

Fig. 232.



copper-pyrites, consisting of a sphenoid  $+\frac{P}{2}$  having its terminal edges replaced by  $oP$ , its summits by faces of  $-\frac{P}{2}$ , while those combination-edges of the two sphenoids which are situated like the terminal edges of  $P$ , are truncated by faces belonging to the pyramid  $P\infty$ . Modified sphenoids also occur in cyanide of mercury, formate of strontium, cholic acid, &c.; but they are not common.

Another hemihedral form  $\frac{mPn}{2}$  is produced by the growth of the alternate faces of the octagonal pyramid (fig. 216). It is a double pyramid with a square base,

but having the sides of the base obliquely inclined to the secondary axes, as may be seen by prolonging the alternate sides of the octagon (fig. 215) till they meet. Such a



form is called a square pyramid of the third order. In like manner are formed square prisms of the third order. Square pyramids of the third order never occur alone, and but rarely in combination. Examples are found in tungstate of lead, tungstate of calcium, and a few other minerals. In native tungstate of calcium (Scheelite) the primary form P occurs, modified by the faces  $2P\infty$  and  $\frac{4P2}{2}$ .

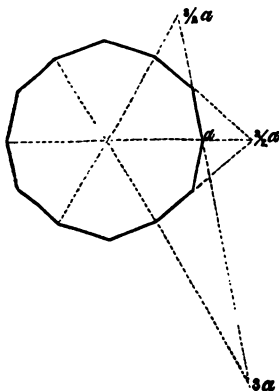
### Hexagonal System.

*Rhombohedral, Monotrimetric System (Drei- und einaxiges, sechsgliedriges, drei- und dreigliedriges System).*—Crystals of this system have three equal secondary axes situated in the same plane and inclined to one another at  $60^\circ$ , and a principal axis at right angles to the plane of the secondary axes. If this axis be placed vertically, the crystal appears differently developed in the vertical and horizontal directions, but equally and similarly developed in the six directions lying in the horizontal plane, viz. at the six extremities of the three secondary axes.

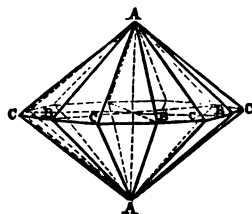
The principal axis is sometimes longer, sometimes shorter than the secondary axes. Its length  $c$  is expressed by referring it to that of a secondary axis as unity.

As three points determine a plane, the position of any face of a crystal in this system is determined by the distances from the centre at which it cuts the principal axis and two of the secondary axes. The most general form is one in which each face cuts two of the secondary axes at unequal distances. Suppose, for example, these distances to be to one another as  $1 : \frac{2}{3}$ . Draw three horizontal axes cutting one another at  $60^\circ$ , as in *fig. 233*, and set off on two of them the distances  $a, \frac{2}{3}a$ . Then, by a construction similar to that described at p. 133, it is found that the horizontal section of the required form is an equilateral dodecagon; and by joining the angular points of this polygon with the extremities of the principal axis (supposed perpendicular to the plane

*Fig. 233.*



*Fig. 234.*



of the paper) we obtain the symmetrical double twelve-sided pyramid (*fig. 234*), bounded by twenty-four scalene triangles  $ABC$ , six of the basal summits,  $B$ , being situated at the extremities of the secondary axes, and six others,  $C$ , half way between. Such forms occur in combination, but not singly.

The general formula of the solid thus determined is  $a : na : pa : c$ , in which when  $n$  is given,  $p$  is determined. In the preceding figure, where  $n = \frac{2}{3}$ ,  $p$  is found to be equal to 3. There are two particular cases of special importance:—

1. When  $n = 1$ , or the formula becomes  $a : a : pa : c$ . In this case it is easy to see that the twelve sides of the base are reduced to six, and the base becomes a regular hexagon (*fig. 235*), having its angles at the extremities of the secondary axes. Each side meets two contiguous axes at equal distances, as at  $f, k$ , and is parallel to the third, so that  $p = \infty$ , and the formula becomes  $a : a : \infty : c$ . The form thus determined is a double six-sided pyramid (*fig. 236*) bounded by twelve isosceles triangles  $ABB$ , which

*Fig. 235.*

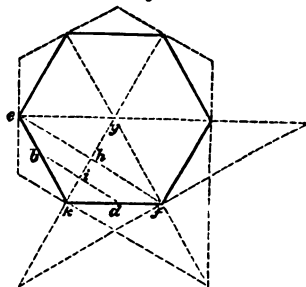
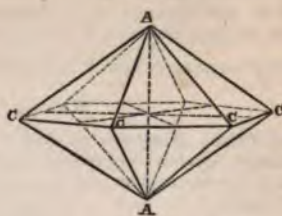


Fig. 236.



Fig. 237.



are acute- or obtuse-angled, according to the ratio of the principal to the secondary axes. Every section perpendicular to the vertical axis is a regular hexagon, like the base, and every vertical section passing through the principal axis is a rhombus.

2. When  $n = 2$ . Each face cuts one of the secondary axes at the distance  $a$  and another at  $2a$ . In this case the construction in *fig. 235* shows that the base of the figure is a regular hexagon, having its sides in the situation of the dotted lines of the figure, each side passing through one of the angles of the former hexagon, and cutting the third secondary axis also at the distance  $2a$  from the centre, so that the formula becomes  $a : 2a : 2a : c$ . The solid figure obtained by joining the angular points of this hexagon with the ends of the principal axis is also a double six-sided pyramid, like *fig. 236*, but differently situated, the ends of the secondary axes passing through the middle points of the sides of the hexagon, and the basal summits  $C$  being situated half way between these axes (*fig. 237*).

When two or more hexagonal pyramids occur together in the same crystal, one replacing the edges or summits of the other, one of them is assumed as the primary form, the secondary axes being supposed to pass through the angles of its base; and of the rest, those which are similarly situated with regard to the axes are called acuter or obtuser pyramids of the first order, while those which are intermediately situated, that is to say, having the middle points of their basal edges at the extremities of the axes, are called pyramids of the second order. The relative lengths of the principal axes of these pyramids are denoted, as in the dimetric system, by placing a multiplier  $m$  before the sign of the principal axis. The abbreviated symbols of the several pyramids are also similar to those used in the dimetric system; thus:—

Primary form	. . . . .	$a : a : \infty a : c = P$
Pyramids of the first order	. . . . .	$a : a : \infty a : mc = mP$
Pyramids of the second order	. . . . .	$a : 2a : 2a : mc = mP_2$
Dodecagonal pyramids	. . . . .	$a : na : pa : mc = mP_n$

If in either of these formulæ  $m = 0$ , the pyramid is reduced to a terminal face  $\infty P$  parallel to the plane of the secondary axes.

If  $m = \infty$ , in either of the formulæ, the corresponding pyramid becomes a vertical prism,  $\infty P$ ,  $\infty P_2$ , or  $\infty P_n$ , of indefinite length.

These prisms and the terminal faces, being unclosed forms, can only occur in combination.

The terms, next obtuser and next acuter pyramid, are used in this system in the same sense as in the dimetric system (p. 134):—*a*. The next obtuser pyramid is that whose faces have the same situation and inclination relatively to the principal axis as the terminal edges of the primary form. For the primary form  $P$ , or  $a : a : \infty a : c$  (*fig. 236*), the next obtuser pyramid is evidently  $a : 2a : 2a : c$  or  $P_2$  (*fig. 236*); and generally, for every hexagonal pyramid  $mP$ , the next obtuser pyramid is  $mP_2$ .

*b*. The next acuter pyramid for the primary form  $P$ , is that whose terminal edges have the same position and inclination relatively to the principal axis as the faces of the primary form. The base of the primary form being the full-lined hexagon (*fig. 235*), the next acuter pyramid is that whose faces meet the principal axis at the same distance  $c$  from the centre, and pass through  $b, d$ , the middle points of the sides  $ck, kf$ , and the corresponding points of the other sides of the same hexagon. Now the line  $bd$  cuts the axis  $gk$  in the point  $i$ , so situated that  $gi = \frac{2}{3} gk$ . Consequently, the formula of this pyramid is  $\frac{2}{3} a : 2 : \frac{2}{3} a : c$ , or  $a : 2a : 2a : \frac{3}{2} c = \frac{3}{2} P_2$ ; and generally, for every pyramid of the first order  $mP$ , the corresponding next acuter pyramid is  $\frac{3}{2} mP_2$ . The terminal edges of a pyramid of the first order  $mP$  are symmetrically truncated by the faces of a pyramid of the second order  $mP_2$ .

The hexagonal and dodecagonal pyramids and prisms above described, are the only



holohedral forms of the hexagonal system. The closed forms (the pyramids) are rarely found alone; examples of simple hexagonal pyramids are found in the compound of grape-sugar and chloride of sodium, and occasionally in quartz. The unclosed forms, viz. the prisms and the terminal faces, occur only in combination.

**Combinations of the Holohedral forms of the Hexagonal System.** Hexagonal pyramids and prisms combine together in the same manner as the corresponding figures of the dimetric system. When two pyramids of the same order occur together, the obtuser of the two acuminate the summits of the more acute, just as in *fig. 220* (p. 134). In like manner, the hexagonal prism occurs acuminate by the pyramid of the same order, the faces of the latter resting on those of the prism, and forming horizontal combination-edges, as in quartz (*fig. 238*). When hexagonal pyramids of different orders occur together, the faces of the one replace the edges and summits of the other, producing truncations, bevellings, or acuminations, according to their relative positions and inclinations. Examples of these combinations, together with the terminal face  $\infty P$ , are seen in *figs. 239, 241, 242*, which are forms of apatite, and *fig. 240*, which is a form of beryl.

Fig. 238.

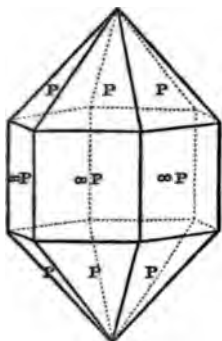


Fig. 239.

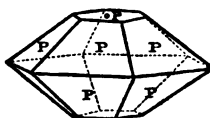
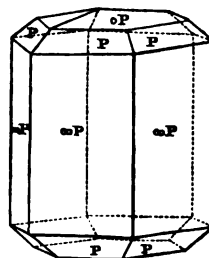


Fig. 240.



The forms  $\infty P$  and  $\infty P$  combined together produce a vertical hexagonal prism with horizontal end-faces. When  $\infty P$  predominates, the prism is reduced to a hexagonal tablet. In *fig. 240* the combination-edges of this form are truncated by the faces  $P$  belonging to a pyramid of the same order as the prism; in *fig. 241* the combination-summits of the same form are truncated by the faces of a pyramid  $2P_2$  of different order. *Fig. 242* affords a good example of the manner in which the different forms making up a complicated combination may be determined. The pyramid whose faces are

Fig. 241.

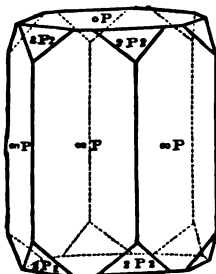
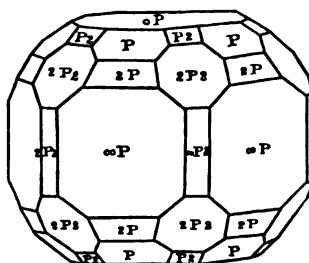


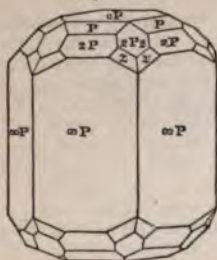
Fig. 242.



denoted by  $P$  is chosen as the primary form, because it is the one to which the other forms may be most conveniently referred. The relation of the faces  $\infty P$ ,  $\infty P$ ,  $\infty P_2$  to this primary form is obvious. The faces of the next obtuser pyramid  $P_2$  are known because they truncate symmetrically the terminal edges of  $P$ ; those of  $2P_2$ , because they truncate the combination-summits of  $\infty P$  and  $\infty P$  (as in *fig. 241*), forming combination-edges which are parallel to the terminal edges of  $P$  (or the combination-edges between  $P$  and  $P_2$ ); and those of  $2P$ , because their terminal edges are symmetrically truncated by  $2P_2$ .

Symmetrical twelve-sided pyramids rarely occur in combination, with all their faces. An example of such a combination is, however, found in beryl (*fig. 243*), in which the twenty-four faces of  $3P_2$  (denoted in the figure by  $z$ ) truncate the edges between  $2P_2$  and  $\infty P$ .

Fig. 243.



In all combinations of hexagonal (and likewise of quadratic forms, the following rule holds good:—Forms which lie in the same direction between the secondary axes intersect one another in horizontal edges, or in such a manner that the upper and lower combination-edges are parallel to each other; but forms which are dissimilarly situated between the secondary axes, intersect one another in inclined edges, the upper and lower not being parallel. Thus the combination-edges between  $\infty P$ ,  $P$ ,  $2P$  and  $\infty P$  (*fig. 242*) are all parallel, as also are those between  $\infty P$  (which is the same as  $\infty P_2$ ),  $P_2$ ,  $2P_2$  and  $\infty P_2$ ; whereas the combination-edges between  $P$  and  $2P_2$ , or  $2P_2$  and  $\infty P$  in the same figure, or between  $3P$  and  $\infty P$  in *fig. 243* are not parallel to one another.

**Hemihedral forms.** The hemihedral forms of the hexagonal system occur more frequently than the holohedral forms, and among them there are two of especial importance, the Rhombohedron derived from the hexagonal pyramid, and the Scaenohedron derived from the dodecahedral pyramid.

1. *Rhombohedral forms.*—Suppose that in a hexagonal pyramid (of the first order, *fig. 236*) the front face above, the right and left faces below, and the three faces alternating with these, are extended till they obliterate the intermediate faces, viz. the front below, the right and left above, &c.; the result will be the rhombohedron (*fig. 244*), a figure bounded by six rhombuses. It has eight summits, which are of two kinds, viz. two terminal summits  $A A$ , formed by the meeting of three terminal edges, and six lateral summits  $D D$ , formed by the concurrence of two lateral edges and one terminal edge. Of the twelve edges, six are terminal, extending from the terminal to the lateral summits, and six lateral, extending in a zig-zag line between the lateral summits. The principal axis joins the terminal summits; the secondary axes unite the middle points of every two opposite lateral edges. The symbol of the rhombohedron would, according to general usage, be  $\frac{P}{2}$ , but it is usually replaced by the shorter symbol  $R$ .

In the rhombohedron formed as above described, one face extends from above forwards, and one edge from below forwards; if however the other alternate faces of the hexagonal prism (*fig. 235*) be supposed to grow, viz. the right and left above, the front below, &c., the result will be a rhombohedron in the opposite position, that is to say, having an edge extending from above forwards and a face from below forwards,

Fig. 244.

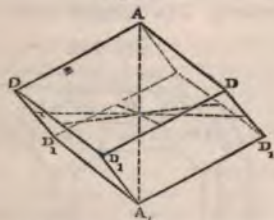
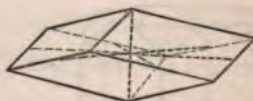


Fig. 245.



as in *fig. 245*. When these opposite rhombohedrons occur together in the same crystal, their faces are distinguished by the signs + and −, the first described rhombohedron, which has a face extending from above forwards, being usually denoted by +  $R$ , the opposite one by −  $R$ .

Rhombohedral forms are acute or obtuse, according as their terminal edges and faces intersect one another at acute or obtuse angles, these inclinations depending of course upon the ratio between the principal and secondary axes. For a particular value of this ratio, the faces and edges meet at right angles, and the rhombohedron has the form of a cube. It is not, however, identical with a cube in anything but external shape: for its edges and summits are of two kinds, and the terminal edges or summits may be modified, while the lateral edges or summits are not, and *vice versa*, whereas in the cube, if any modification occurs, all the corresponding parts must be similarly modified.

When a number of rhombohedrons of different degrees of acuteness occur together,



that one is selected as the primary form in the direction of whose faces the crystal cleaves most easily, and this rhombohedron being denoted by  $+R$  (that is to say, being so placed that one face of the primary form extends from above forwards), the others are denoted by  $\pm mR$ , the number  $m$  denoting the ratio of the principal axis of each rhombohedron to that of the primary form. This ratio is always very simple. (See *Calcspar*, i. 721.)

When two rhombohedrons of the same order occur together, the more obtuse acuminate the terminal summits of the more acute, as in *fig. 246*, a form of calcspar in which the terminal summits of  $+4R$  are acuminate by  $+R$ ; but when rhombohedrons of different orders occur together, the edges or summits of the one are truncated by the faces of the other, as in *figs. 247—249*. A rhombohedron by which the terminal edges of the primary form are symmetrically truncated, is called the next

Fig. 246.

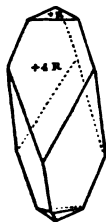


Fig. 247.

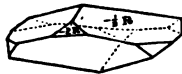


Fig. 248.

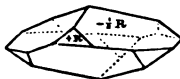
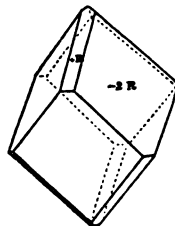


Fig. 249.



obtuser rhombohedron of that form; and the rhombohedron whose terminal edges are symmetrically truncated by the faces of the primary form is called the next acuter rhombohedron of that form. Of any rhombohedron  $\pm mR$ , the next obtuser is  $\mp \frac{1}{2}mR$ , and the next acuter is  $\mp 2mR$ . In *fig. 249*,  $+R$  is the next obtuser rhombohedron of  $-2R$ . Examples of rhombohedrons thus related are found in calcspar (i. 721), also in chabasite (i. 843).

The two opposite rhombohedrons  $+R$  and  $-R$ , formed from the same hexagonal pyramid, are often combined together, and when they are equally developed, produce a combination undistinguishable in form from the holohedral hexagonal pyramid. There are, however, essential differences between the two: sometimes the faces of the opposite rhombohedrons differ in lustre or in mode of striation; sometimes the crystal cleaves in directions parallel to one set of faces and not to the other; frequently also the manner in which the faces and edges are modified affords the means of distinction: thus the horizontal combination-edges of quartz,  $\infty P$ ,  $P$  (*fig. 238*), are sometimes truncated by the faces  $3P$ ; but this modification does not affect the whole of these edges, but only the alternate ones, *e. g.* the front combination-edge above, the right and left below, &c., whereas, if the crystal were holohedral, all these edges would be modified alike (*fig. 258*).

The terminal face  $oR$  truncates the terminal summits of a rhombohedron, as in corundum (*fig. 146*, p. 86); if the face  $oR$  predominates greatly, the crystal is reduced to a tablet like *fig. 147*.

The more the principal axis of a rhombohedron increases relatively to the secondary axes, the smaller do the angles at the terminal edges become, and the more nearly do those of the lateral edges approach to  $120^\circ$ , that is to say, to the inclination of the faces of a hexagonal prism (see *TABLE*, vol. i. p. 721). And finally, if the principal axis becomes infinite, the faces of the rhombohedron become parallel to it, and the figure becomes a hexagonal prism identical with  $\infty P$ ; in rhombohedral combinations it is however denoted by  $\infty R$ .

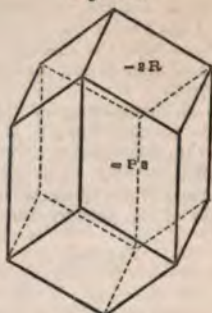
Rhombohedral forms occur in combination with hexagonal prisms. With a predominant hexagonal prism of the first order,  $\infty P$ , or  $\infty R$ , a rhombohedron (of either order) combines in such a manner as to produce three-faced terminations, the acumination-faces resting symmetrically on the faces of the prism, and disposed alternately above and below, as in calcspar  $\infty R$ ,  $-\frac{1}{2}R$  (*fig. 250*); on a prism of the second order,  $\infty P_2$ , a rhombohedron likewise forms three-faced acuminations, with its faces likewise disposed alternately above and below, but resting symmetrically on the edges of the prism, as in *fig. 251*, which is a form of diopase.

**2. Scalenoehedrons.**—This form, represented in *figs. 252, 253*, is produced by the extension of the alternate faces of the double twelve-sided pyramid, *fig. 234*, p. 137. It is bounded by twelve scalene triangles, has two six-faced terminal summits, six four-faced lateral summits, and eighteen edges of three different kinds, viz. six longer and six shorter edges between the terminal and lateral summits, and six lateral edges forming

Fig. 250.



Fig. 251.



a zigzag between the lateral summits. The middle points of these lateral edges are situated at the extremities of the secondary axes, so that these edges have the same relative situation as the lateral edges of a rhombohedron; and in fact, the easiest way of conceiving the generation of a scalenohedron is to suppose the principal axis of a rhombohedron to be elongated, and straight lines drawn from the extremities of this elongated axis to the lateral summits of the rhombohedron.

A scalenohedron is determined by the dimensions and position of the rhombohedron from which it may be conceived to be formed, and by the number of times that the axis of that rhombohedron must be multiplied to produce it; the latter is indicated by placing a superior figure to the right of the symbol of the rhombohedron; thus a scalenohedron whose vertical axis is  $n$  times that of its generating rhombohedron  $mR$ , is denoted by the symbol  $mR^n$ .

Fig. 252.

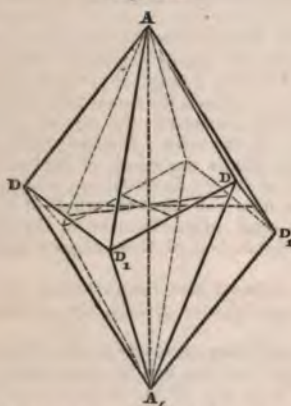


Fig. 253.



Scalenohedrons are further distinguished as  $+$  or  $-$ , according to the position or order of the generating rhombohedron, or according as they are produced by the extension of one or the other set of alternate faces of the primitive dodecahedral pyramid. The opposite forms are shown in *figs.* 252, 253. The form  $+R^3$  occurs in calcspar, constituting the variety called *dog's-tooth spar* (*fig.* 123, vol. i. p. 722).

The terminal summits of a scalenohedron are often acuminate with three faces of the rhombohedron from which the scalenohedron may be supposed to be derived, the combination-edges being parallel to the lateral edges of the scalenohedron, as in *fig.* 254, which is also a form of calcspar. The lateral summits are also frequently truncated by the faces of the first hexagonal pyramid  $\infty P$ , and the lateral edges by those of the second hexagonal prism  $\infty P_2$ .

3. *Other hemihedral forms.*—The double dodecahedral pyramid  $mPn$  (*fig.* 232) may become hemihedral in the same manner as the double eight-sided prism of the quadratic system (p. 133), viz. by the extension of each alternate pair of faces meeting in a lateral edge. The figure thus produced is a double six-sided prism of the third order. Every dodecahedral pyramid yields two such hexagonal pyramids of the third order, according as one or other set of alternate faces is supposed to grow. The base



Fig. 254.

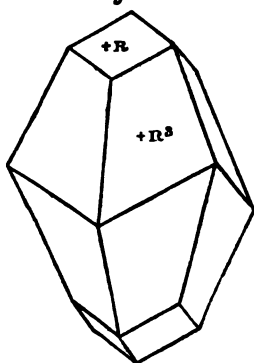
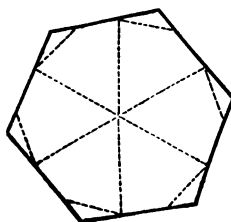


Fig. 255.



of one of these pyramids is represented by the full lines in (fig. 255), that of the other by the dotted lines. The lateral summits of each of these pyramids are situated between the secondary axes, and at unequal distances from each pair of axes.

Hexagonal prisms of the third order,  $\frac{\infty Pn}{2}$ , are produced in like manner from the dodecahedral prism.

This kind of hemihedry is strikingly exhibited in apatite. In fig. 241 (p. 139) the combination-edge, which each face of  $2P2$  forms with the two contiguous faces of  $\infty P$ , may be truncated by a face of a dodecahedral pyramid, as in beryl (fig. 243, p. 140), where the twenty-four small faces denoted by  $s$  belong to the pyramid  $3P\frac{3}{2}$ . In apatite, however, only half of these combination-edges are thus truncated, viz. those which each face  $2P2$  forms with the face  $\infty P$  to the left of it, while the one to the right remains unaltered (fig. 256). The truncation-faces, therefore (represented by  $m$  in fig. 256), belong to the hemihedral form  $\frac{3P\frac{3}{2}}{2}$ . In like manner, of the two combination-edges

Fig. 256.

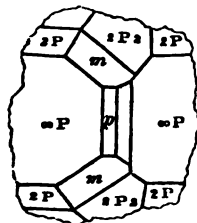


Fig. 257.

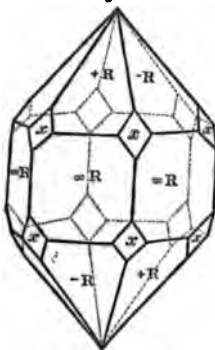
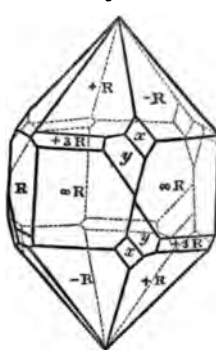


Fig. 258.



which each face  $\infty P2$  forms with the two contiguous faces  $\infty P$  (fig. 242), one only is truncated, the faces  $p$  (fig. 256) belonging to the hexagonal prism  $\frac{\infty P\frac{3}{2}}{2}$ .

The hexagonal pyramid of the second order (p. 138) may also become hemihedral by the obliteration of half of its faces in the manner just described, the resulting figure being a double triangular pyramid  $\frac{mP2}{2}$ , having an equilateral triangle for its base. It never occurs alone, but is found in quartz, replacing half of the summits formed by the faces of the two opposite and equally developed rhombohedrons  $+R$  and  $-R$  (p. 140) and the hexagonal prism  $\infty R$ . If the crystal were holohedral, the whole of these summits would be thus replaced, and the combination would be that represented in fig. 267, where the faces  $x$  belong to the second hexagonal pyramid  $2P2$ . In reality, however, only half these summits are thus replaced, as represented by the faces  $x$  or  $\frac{2P2}{2}$  in fig. 258.

Hexagonal prisms of the second order likewise become hemihedral by the obliteration of half their faces alternately situated, producing triangular prisms.

*Tetartohedry*.—Quartz affords a remarkable example of a combination in which only one-fourth of the possible faces are present (p. 121). The combination-edges between the faces  $x$  and  $\infty R$  are often truncated by faces  $y$ , belonging to a dodecagonal pyramid,  $6P_2^3$ ; but of the twenty-four faces belonging to this form, six only are present, as shown in fig. 258. Quartz likewise exhibits other forms of tetartohedral development.

### Trimetric or Rhombic System.

*Prismatic, Right prismatic, Orthotypic, Isoclinic, Holohedro-rhombo-trimetric System (Zwei- und zweigliedriges, ein- und einaxiges System).*

Crystals belonging to this system have three rectangular axes, all of different lengths; in other words, they are unequally developed in three directions at right angles to each other. The axes are likewise dissimilar in this respect, that they terminate in dissimilar parts of the crystal.

The three axes of a trimetric crystal are therefore singular axes (p. 120), and there is no reason for considering either of them as a principal axis rather than the others.

It is, however, convenient to regard as the principal axis, that one of the three in the direction of which the crystal is to the greatest extent prismatically developed, or to which the greatest number of faces are parallel. This axis we shall suppose to be placed vertically, and denoted by the letter  $c$ . Of the two secondary axes, the shorter, called the brachydiagonal ( $a$ ), will be supposed to extend from left to right; the longer, or macrodiagonal ( $b$ ), from back to front (fig. 259). The relative lengths of the three axes vary greatly in different crystals belonging to this system; in sulphur, the proportion of  $a : b : c$  is 0.81 : 1 : 1.90; in neutral sulphate of potassium, it is 0.746 : 1 : 0.573.

A plane passing through any two of the axes is called a principal section, and is further distinguished as basal when it passes through the two secondary axes, macrodiagonal when it passes through the principal and longer secondary axis, brachydiagonal when it passes through the principal and shorter secondary axis.

The most general, and at the same time the simplest form of a trimetric crystal, whose faces meet the axes at the distances  $a b c$  from the centre is a symmetric eight-sided pyramid\* (figs. 259, 260), having its summits at the extremities of the axes. Its faces are all scalene triangles. Its twelve edges are of three kinds, viz. four lateral edges,  $B C$ , situated in the basal principal section, four terminal edges,  $A C$ , in the macrodiagonal, and four terminal edges,  $A B$ , in the brachydiagonal principal section. All the three principal sections are rhombuses, but with different angles. Hence this form is called a rhombic pyramid. The six summits are also of three kinds, viz. two terminal summits,  $A$ , two lateral summits,  $B$ , at the extremities of the brachydiagonal, and two lateral summits,  $C$ , dissimilar to the latter, at the extremities of the macrodiagonal.

The general symbol of a rhombic pyramid is:

$$a : b : c, \text{ or } P.$$

The particular form varies with the ratios between the axes. When two or more rhombic pyramids occur together in the same crystal, they are distinguished by symbols similar to those used in the preceding systems.

If the secondary axes remain the same and the principal axis varies, the formula becomes:

$$a : b : mc, \text{ or } mP,$$

\* It is important to observe how the interpretation of a crystallographic formula varies according to the law of symmetry of the crystal, that is to say, according to the system to which it belongs. In the trimetric system, the formula  $a : b : c$  represents a figure with only eight sides, one in each octant, because, the dimensions of the crystal being different in the directions of all three axes, each of the distances  $a, b, c$ , is measured along one axis only; but in the dimetric system, whose forms are equally developed in the directions of the two secondary axes, each of the distances  $a, b$ , must be set off on each of those axes, whence there results a figure having twice the preceding number of faces, that is to say, sixteen (p. 133); and in the monometric system, which includes the forms equally developed in the direction of all three axes, the process last described has to be repeated three times, regarding each axis in turn as a principal axis; hence results a figure having  $3 \times 16 = 48$  sides (p. 127).

Fig. 259.

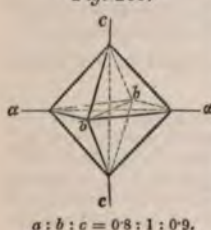
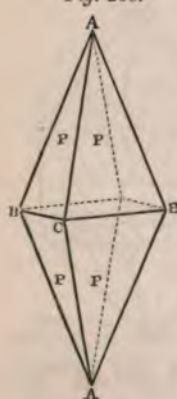


Fig. 260.





the pyramid becoming more acute or more obtuse in the vertical direction, according as  $m$  is greater or less than 1.

If the macrodiagonal varies, while the other two axes remain the same, the formula becomes :

$$a : nb : c, \text{ or } \bar{P}n.$$

and if the principal axis varies at the same time :

$$a : nb : mc, \text{ or } m\bar{P}n,$$

which represents pyramids more or less elongated in the direction of the axis  $b$ , according as  $n$  is greater or smaller. In like manner, the variation of the brachydiagonal gives the forms :

$$na : b : mc, \text{ or } m\bar{P}n.$$

When  $m$  or  $n$  becomes infinite, the faces become parallel to the principal or one of the secondary axes, and indefinitely elongated in the corresponding direction.

$$a : b : \infty c, \text{ or } \infty P$$

represents a rhombic prism, whose faces meet the secondary axes at the distances  $a, b$  from the centre (these axes forming its diagonals), and extend indefinitely in the direction of the vertical axes.

$$a : nb : \infty c, \text{ or } \infty \bar{P}n, \\ \text{and } na : b : \infty c, \text{ or } \infty \bar{P}n$$

likewise represent indefinite vertical prisms, but with different horizontal sections

$$a : \infty b : mc, \text{ or } m\bar{P}\infty$$

represents, in like manner, a series of prisms whose faces are parallel to the macrodiagonal, and whose sections perpendicular to that axis are rhombuses, having  $a$  and  $mc$  for their diagonals.

$$\infty a : b : mc, \text{ or } m\bar{P}\infty$$

represents a series of prisms whose faces extend indefinitely parallel to the brachydiagonal, and whose sections perpendicular to that axis are rhombuses, having  $b$  and  $m$  for their diagonals.

The prisms  $m\bar{P}\infty$  and  $m\bar{P}\infty$ , whose faces are parallel to one of the secondary axes, are called domes (from *domus*, a house), because they terminate the crystal in the vertical direction like pitched roofs (see *figs.* 266—268), and are further distinguished as macrodiagonal or brachydiagonal domes, according to the direction in which they extend. The formula

$$a : \infty b : \infty c, \text{ or } \infty \bar{P}\infty$$

represents a pair of indefinitely extended planes passing through the extremities of the brachydiagonal, and at right angles thereto, or parallel to the macrodiagonal section; and

$$\infty a : b : \infty c, \text{ or } \infty \bar{P}\infty$$

represents, in like manner, a pair of infinitely extended planes parallel to the brachydiagonal section, and passing through the extremities of the macrodiagonal.

When  $c = 0$  (whatever may be the lengths of the secondary axes), the form is reduced to a single plane, the terminal face  $oP$ , parallel to the basal section.

The prisms and the terminal planes, being unclosed forms, occur only in combination.

The following table\* exhibits a summary of all the forms of the trimetric system

\* The formulæ above given for this and the preceding systems are those originally proposed by Naumann and adopted by Kopp and many other writers. Dana uses similar formulæ, but shortens them by suppressing the  $P$ , and expressing infinity by  $i$  or  $l$ , instead of  $\infty$ . The primary form  $a:b:c$  is denoted by  $l$ ; the other forms in the manner shown in the following table:—

Naumann.		Dana.
$P$	=	$l$
$mP$	=	$m$
$\infty P$	=	$l$
$m\bar{P}n$	=	$m\bar{n}$
$m\bar{P}a$	=	$m\bar{n}$
$m\bar{P}\infty$	=	$m\bar{i}$
$m\bar{P}\infty$	=	$m\bar{l}$
$\infty \bar{P}\infty$	=	$i\bar{i}$
$\infty \bar{P}\infty$	=	$l\bar{l}$
$oP$	=	$0$

The expressions used in the monometric, dimetric, and hexagonal systems are of similar character. These formulæ are certainly shorter than those of Naumann, and the  $P$  in the latter (or the  $O$  in the monometric system) does not add much to the sense; but on the other hand, Naumann's formulæ strike the eye better, and are more distinct from anything else in the text than the shorter formulæ of Dana. [For the mode of representation adopted by Miller, see the new edition of *Phillips's Mineralogy*, by W. J. Brooke and W. H. Miller. London, 1852.]

[ $m$  denotes a multiplier varying in magnitude from 0 to  $\infty$ ;  $n$  a multiplier varying from 1 to  $\infty$ ]:—

$m < 1$			$m > 1$		
$\circ P \infty = \circ P$	$\bar{P} \infty$	$P \infty$	$m P \infty$	$\infty \bar{P} \infty$	
$\circ P n = \circ P$	$m \bar{P} n$	$\bar{P} n$	$m P n$	$\infty P n$	
$\circ P = \circ P$	$m P$	$P$	$m P$	$\infty P$	
$\circ P n = \circ P$	$m \bar{P} n$	$\bar{P} n$	$m P n$	$\infty \bar{P} n$	
$\circ P \infty = \circ P$	$m \bar{P} \infty$	$\bar{P} \infty$	$m P \infty$	$\infty \bar{P} \infty$	

**Combinations.** The pyramids, prisms, domes, and end-faces of the trimetric system form a large number of combinations, of which the following may be regarded as the most important.

The terminal edges of the primary form are acuminated by those of an obtuser pyramid of equal base, the combination-edges being parallel to the lateral edges of the primary form, as in *fig. 261*, which is a form of sulphur. The brachydiagonal dome  $\bar{P} \infty$  truncates symmetrically the macrodiagonal terminal edges (*fig. 262*), and in like manner, the macrodiagonal dome  $P \infty$  produces symmetrical truncation of the brachydiagonal terminal edges, the combination-edges being in both cases parallel to each other. Acuter and obtuser domes ( $m P \infty$  or  $m \bar{P} \infty$ , for which  $m > 1$ ) would likewise replace the terminal edges wholly or partially, the combination-edges converging towards the terminal summits when the dome is more acute than the primary form ( $m > 1$ ), and diverging in the contrary case.

The terminal summits of the primary form are truncated by the basal end-faces  $\circ P$  (*fig. 262*); the macrodiagonal summits by the brachydiagonal end-faces  $\infty \bar{P} \infty$ ; and the brachydiagonal summits by the macrodiagonal end-faces  $\infty P \infty$ . If these two pairs of end-faces predominate together with the primary form, the result is a combination like *fig. 263*, a form of uranic nitrate.

Fig. 261.

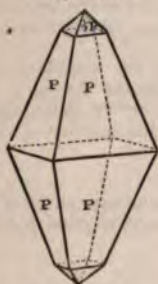


Fig. 262.



Fig. 263.



The lateral edges of the primary form are symmetrically truncated by the prism  $\infty P$  having the same base or secondary axes; if the latter predominates, the pyramid  $P$  forms 4-faced summits to it, the combination-edges being parallel to the base and to each other, as in sulphate of zinc (*fig. 264*); but in the combination of a prism and a pyramid having different bases (*i. e.* having their secondary axes in different ratio to each other), the combination edges are inclined to one another, as in *fig. 271*, a form of sulphate of potassium, which exhibits the combination of  $P$  with  $\infty P2$ .

The edges of a prism in which the macrodiagonal terminates (the acuter edges in  $\infty P$ ) are truncated by the brachydiagonal end-faces  $\infty \bar{P} \infty$ , and the brachydiagonal edges by the macrodiagonal end-faces  $\infty P \infty$  (*fig. 275*). The acuter edges of the prism  $\infty P$  are bevelled by the faces of a prism  $\infty \bar{P} n$  of different transverse section (*e. g.* by  $\infty \bar{P} 2$ , in *fig. 265*, a form of topaz), in which it may also be observed that the forms  $P$  and  $\infty P$ , which have the same base, form parallel combination-edges; whereas  $P$  and  $\infty P2$ , which have different bases, form combination-edges inclined to each other. In like manner, the obtuse angles of  $\infty P$  are bevelled by a prism  $\infty P n$  of different horizontal section.

The prism  $\infty P$  is symmetrically truncated at the end by  $\circ P$ , and it is bevelled by a brachydiagonal or macrodiagonal dome; the bevelled faces formed by the macrodiagonal dome rest on the prismatic edges in which the brachydiagonal terminates, as in *fig. 266*, which represents formate of barium; and the bevelled faces formed by a brachydiagonal dome rest on the prismatic edges in which the macrodiagonal terminates, as in acid malate of calcium (*fig. 267*).



Fig. 264.

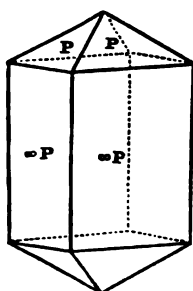
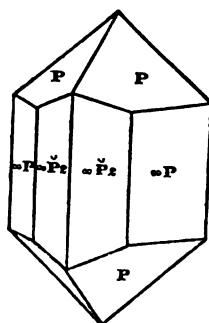


Fig. 265.



The edges of  $\infty P$  may also be replaced by end-faces, on which the beveling-faces of the dome then rest. Several domes of the same kind may also occur together, as in *fig. 268*, a form of nitre, exhibiting the faces  $\infty P$ ,  $\infty \bar{P}$ ,  $2\bar{P}\infty$ ,  $\bar{P}\infty$ ,  $P$ .

In selecting the primary form and the principal axis of a complicated trimetric combination, the following considerations must be taken into account. When pyramidal and prismatic faces occur together, the pyramid is regarded as the primary form. When

Fig. 266.

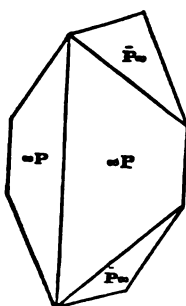


Fig. 267.

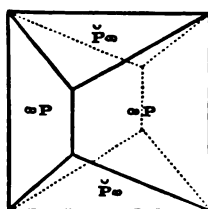
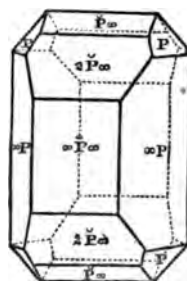


Fig. 268.



several pyramids occur together, the most predominant is regarded as the primary form, unless the greater number of faces can be more conveniently referred to one of the other pyramids. When trimetric crystals are bounded only by prismatic and dome-faces, the predominant faces are regarded as belonging to the prism or the domes which have the simplest formula ( $\infty P$ ,  $\bar{P}\infty$ , or  $\bar{P}\infty$ ), and the axes of the primary form are determined accordingly.

It has already been observed that the principal axis in a trimetric crystal is merely relative, not absolute, as in the dimetric and hexagonal systems, and that the axis in the direction of which the crystal is most developed, or to which the greater number of edges are parallel, is usually regarded as the principal. When crystals are partially imbedded in a matrix, or attached to its surface, the most completely developed extremity is usually regarded as the upper, and the axes are determined accordingly. When a crystal exhibits only one set of pyramidal faces, these are regarded as primary, and the two axes which are most nearly equal are regarded as the secondary axes. If a crystal exhibits only one pyramid and one kind of end-face, the axes are chosen so that these faces may be represented by  $\infty P$ ; if it has two kinds of end-face besides the pyramid, it will appear symmetrically placed if one kind of end-face is regarded as  $\infty \bar{P}\infty$ , the other as  $\infty \bar{P}\infty$ .

When a trimetric crystal exhibits prismatic faces, the axis to which these faces are parallel is usually regarded as the principal; if it has prismatic faces parallel to several axes, that axis is chosen as the principal in the direction of which the faces are most developed. This rule may often appear of uncertain application, because different crystals of the same substance may be most developed in different directions; but when the choice of a principal axis has once been made, it must be maintained through-

out the description of the crystal, however much particular modifications may be developed in other directions.

The following are examples of the determination of somewhat complicated crystals belonging to the trimetric system.

Sulphate of potassium,  $K_2SO_4$ , exhibits considerable variety of form. The crystals exhibit, for the most part, the most decided prismatic development in the direction which, in the following figures (269 to 275), is placed vertically. The primary form is a rhombic pyramid  $c a b c' a'$  (fig. 269), whose axes, represented by the dotted lines, are in the proportion  $a : b : c = 0.7464 : 1 : 0.5727$ . This primary form is often modified by the faces of the vertical prism  $\infty P2$ . The horizontal axes of this prism are  $2a$  and  $b$ , or, what comes to the same thing,  $a$  and  $\frac{1}{2}b$ . Two of its faces will therefore pass through the points  $a, a'$  and a line  $d e$  drawn through the middle point of  $O b$ , parallel to the vertical axis,—or at least will be parallel to planes so drawn. If they pass exactly through the point  $a$  and  $\frac{1}{2}b$ , they will intersect the faces  $P$  in the lines  $a d, a' d, a e, a' e$ , and will produce a form ( $\infty P . \infty P2$  equally developed) scarcely distinguishable from a hexagonal pyramid. That its faces are really of two kinds may, however, be known from the fact that the faces  $\infty P2$  appear sometimes less, sometimes more developed in crystals of the same salt, as in figs. 270, 271. Moreover, the faces  $\infty P2$  in fig. 269 are isosceles, while the faces  $P$  are scalene triangles; and of the six edges  $c a, d e, e c', \&c.$ , lying in the macrodiagonal principal section (which might be taken for lateral edges of a hexagonal prism), two belong to the prism  $\infty P2$ , and the four others are terminal edges of the pyramid  $P$ . The former meet at an angle of  $112^\circ 41'$ , the latter at  $112^\circ 22'$ ; the former may be replaced by cleavage-planes, the latter cannot. The twelve edges,  $c a, c a', d a, d a', \&c.$ , which might be taken for the ter-

Fig. 269.

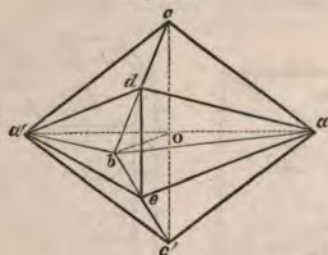


Fig. 270.



minal edges of a hexagonal prism are also dissimilar, four, viz.  $c a, c a', c' a, c' a'$ , being terminal edges of  $P$  situated in the brachydiagonal principal section, and the rest combination-edges between  $P$  and  $\infty P2$ .

In fig. 272, the macrodiagonal terminal edges of  $P$  are truncated by the faces of a prism forming parallel combination-edges, therefore  $\tilde{P} \infty$ ; and the edges of  $\infty P2$ , through which the macrodiagonal passes, are truncated by  $\infty \tilde{P} \infty$ . The combination thus produced is very much like the hexagonal combination  $\infty P . P$  found in quartz (fig. 238, p. 139). Were this the only known form of sulphate of potassium, the axis which in fig. 272 appears as the brachydiagonal, would be taken for the principal axis, because it is the one in which the crystal exhibits the most decided prismatic develop-

Fig. 271.

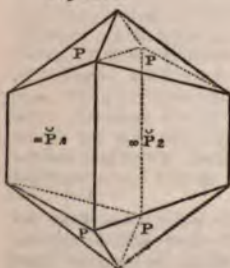
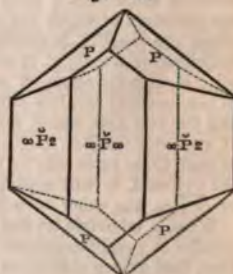


Fig. 272.



Fig. 273.



ment. This axis is, however, not actually regarded as the principal, because a perfectly similar combination is known, viz. fig. 273 (the same as the preceding without



Fig. 274.

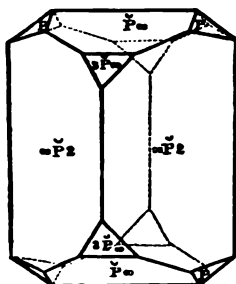
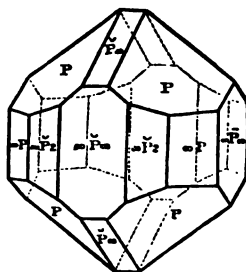


Fig. 275.



$\bar{P}\infty$ ), in which the prismatic faces  $\infty\bar{P}\infty$ ,  $\infty\bar{P}2$ , parallel to the vertical axis, are by far the most predominant. In *fig. 274* the faces  $\infty\bar{P}2$  and  $\bar{P}\infty$  predominate, so that the  $P$ -faces become very small, but are still large enough to show that the faces of the vertical prism do not form horizontal combination-edges with them, and consequently that this prism must have a different base (or its secondary axes in different proportions) from  $P$ ; also that the predominant brachydiagonal dome forms with  $P$  combination-edges parallel to the macrodiagonal section (and to each other), and therefore that this dome is  $\bar{P}\infty$  (not  $m\bar{P}\infty$ , where  $m$  is greater or less than unity). The crystal has likewise small triangular faces belonging to a brachydiagonal dome more acute than  $\bar{P}\infty$ ; angular measurement shows them to be  $3\bar{P}\infty$ .

Lastly in *fig. 275*, the primary form  $P$  is combined with  $\bar{P}\infty$ ,  $\infty\bar{P}\infty$ ,  $\infty\bar{P}\infty$  which faces are easily determined, and two vertical prisms, one of which forms horizontal combination-edges with  $P$ , and is therefore  $\infty\bar{P}$ , while the other evidently comes under the formula  $\infty\bar{P}n$ , and is found by angular measurement to be  $\infty\bar{P}2$ .

A remarkable example of the various directions in which crystals of the same substance may be prismatically developed, is afforded by native sulphate of barium,  $\text{BaSO}_4$ . One of its forms is shown in *fig. 276*, which exhibits several vertical prismatic faces; and as the same faces occur more or less developed in several other forms of the same substance, this axis is regarded as the principal. Regarding the pyramidal faces  $P$  as the primary form, two domes may be observed, which truncate symmetrically the acute and obtuse edges of  $P$ : these domes are therefore  $\bar{P}\infty$  and  $\bar{P}\infty$ ; but the vertical prism whose faces form with  $P$  combination-edges not parallel to each other, is a secondary prism of the general form  $\infty\bar{P}n$  (where  $n > 1$ ), because the combination-edges which it forms with  $P$  diverge towards the macrodiagonal principal section [a prism  $\infty\bar{P}n$ , in which  $n < 1$  would form with  $P$  combination-edges converging towards that section]. Angular measurement shows that this prism is  $\infty\bar{P}2$ . The end-face  $\infty\bar{P}\infty$  is known by the horizontality of its combination-edges with  $\bar{P}\infty$ . The faces thus determined,  $\infty\bar{P}2$ ,  $\infty\bar{P}\infty$ ,  $\bar{P}\infty$ ,  $P\infty$ , also occur alone and with various degrees of relative development, producing crystals of very different character. The face  $\infty\bar{P}2$  predominates in *fig. 277*;  $\bar{P}\infty$  in *fig. 278*;  $P\infty$  in *fig. 279*; and accordingly

Fig. 276.

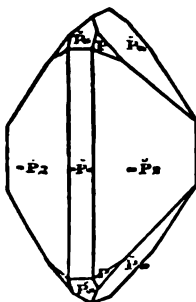


Fig. 277.

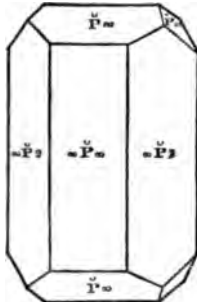
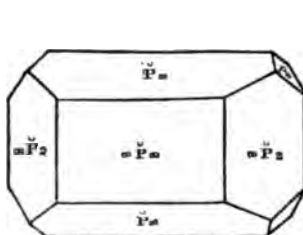
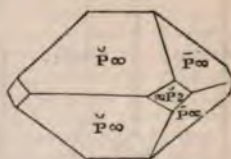


Fig. 278.



the combination is prismatically elongated in the direction of the vertical axis in *fig. 277*, of the brachydiagonal in *fig. 278*, and of the macrodiagonal in *fig. 279*. In

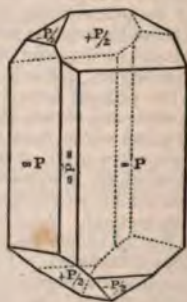
short, whichever axis may be chosen as the principal, crystals of the mineral will be found which are prismatically elongated in the direction of one of the secondary axes. *Fig. 280* is a combination similar to *fig. 279*, but without  $\infty P\infty$ ; the dominant face

*Fig. 279.**Fig. 280.*

is  $\check{P}\infty$ , as in *fig. 278*; but  $P\infty$  is likewise more developed;  $\infty P2$  is subordinate as in *fig. 279*.

The choice of a primary form and principal axis for any substance is binding, not only for all crystals of that particular substance, but likewise for all that are isomorphous with it; thus the crystals of celestine ( $\text{Sr}^2\text{SO}^4$ ) must be referred to the same primary form and principal axis as those of heavy spar ( $\text{Ba}^2\text{SO}^4$ ), although celestine generally exhibits a form like *fig. 280*, prismatically elongated in the direction of the macrodiagonal. The advantage of referring all isomorphous crystals to the same primary form and principal axis is, that the corresponding faces are then more easily made out and expressed by analogous symbols.

**Hemihedral Forms.** Rhombic pyramids, by the growth of their alternate faces

*Fig. 281.**Fig. 282.*

till the others disappear, give rise to rhombic sphenoids, in the same manner as quadratic prisms produce quadratic sphenoids (p. 136). A rhombic sphenoid is bounded by four scalene triangles, and of its six edges, only the opposite pairs are similar to each other.

Rhombic sphenoids have hitherto been observed only in combination. A remarkable instance of such a combination is exhibited in *fig. 281*, the ordinary form of sulphate of magnesium ( $\text{Mg}^2\text{SO}^4 + 7\text{H}^2\text{O}$ ), in which the vertical prism  $\infty P$  is terminated by dome-shaped summits placed in opposite directions above and below. In sulphate of zinc ( $\text{Zn}^2\text{SO}^4 + 7\text{H}^2\text{O}$ ), which is isomorphous with sulphate of magnesium, both sets of alternate  $P$ -faces appear together, but developed in different degrees, as in *fig. 282*.

### Monoclinic System.

*Monoclinometric, Monoclinohedral, Oblique, Oblique prismatic, Clinorhombic, Augitic System (Zwei- und eingliedriges, hemiedrisch-rhombisch-trimetrisches System).*

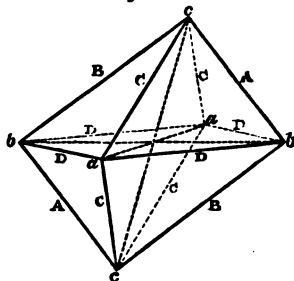
The forms of this system have three unequal axes, like those of the rhombic system, but differ from the latter in having two of their axes obliquely inclined to one another, while the third is at right angles to the other two. Each of these axes is a singular



axis (p. 120), and therefore the choice of a principal axis is to a great extent arbitrary, as in the rhombic system; but it is usual to consider one of the oblique axes as the principal, because most crystals belonging to the system are prismatically developed in the direction of one of these oblique axes. Of the two secondary axes, that which is obliquely inclined to the principal axis is called the clinodiagonal, and that which is perpendicular to the other two, the orthodiagonal.

In representing monoclinic crystals, the secondary axes are supposed to be situated in a horizontal plane, the clinodiagonal  $b$   $b$  (fig. 283) extending from left to right, the orthodiagonal  $a$   $a$  from back to front, and the principal axis  $c$   $c$  from right above to left below. In this mode of representation, the principal axis and clinodiagonal appear of their true relative lengths, and at their true inclination ( $= 75^\circ$  in the figure); but the orthodiagonal is fore-shortened and appears oblique to the other two axes, though really perpendicular. Sections passing through the planes of any two axes are called principal sections, as in the preceding system, and are distinguished as basal, clinodiagonal, and orthodiagonal, according to the axes through which they pass.

Fig. 283.



For every monoclinic crystal, the ratio of the three axes (the length of the clinodiagonal being taken as unity) and the inclination  $L$  of the principal axis to the clinodiagonal, have to be determined by angular measurement and calculation. The value of  $L$  varies considerably in different crystals; in some it is nearly  $90^\circ$ , while in others it differs considerably therefrom. For ferrous sulphate,  $a : b : c = 0.848 : 1 : 1.267$ ;  $L = 75^\circ 40'$ ; for felspar,  $a : b : c = 1.519 : 1 : 0.844$ ;  $L = 63^\circ 53'$ .

The primary form in this system is the monoclinic pyramid (fig. 283) bounded by eight scalene triangular faces, which meet the axes at the distances  $a$ ,  $b$ ,  $c$  from the centre. This, however, is not a simple form, for its faces are of two kinds; four of them, which are opposite to the acute angles of the axial system and meet in the edges  $A$  above and below, are equal and similar to each other; and the four which are opposite to the obtuse angles of the axes and meet in the edges  $B$ , are also equal and similar to each other, but unequal and dissimilar to the former. These two sets of faces may occur in combinations quite independently of each other, and a monoclinic crystal may be cleavable in directions parallel to one set of faces but not to the other. Neither of them by itself constitutes a closed form; but the four faces of either set, if sufficiently extended, form an endless prism obliquely inclined to the principal axis and the clinodiagonal.

A complete monoclinic pyramid has two terminal summits  $c$   $c$ , and four lateral summits, two at the ends of each secondary axis. It has four similar lateral edges  $D$ , joining the lateral summits, four similar terminal edges  $C$ , joining the extremities of the principal axis and orthodiagonal; and four other terminal edges joining the ends of the principal axis and clinodiagonal, the shorter ones,  $A$ , being opposite to the acute angles of the axes, and the longer,  $B$ , opposite to the obtuse angles.

The primary monoclinic pyramid is denoted by the symbol  $P$ ; but as its two sets of faces are dissimilar, and may occur independently of each other, the four faces meeting in the edges  $A$  are denoted by  $+P$ , and the four which meet in the edges  $B$  by  $-P$ ; the closed pyramid containing all the eight faces is  $\pm P$ .

From this primary form, others may be derived, as in the rhombic system, by variation of the length of either of the three axes. The variation of the principal axis is denoted, as before, by placing before the  $P$  a multiplier  $m$ , which may have all values from 0 to  $\infty$ . The variations of the secondary axes are denoted by placing after the sign  $P$ , a number  $n$ , which may have all values from 1 to  $\infty$ , the formula being enclosed in brackets when the variation refers to the clinodiagonal, not enclosed when it refers to the orthodiagonal.

$m = 0$  gives the end-faces  $oP$ , which cut the principal axis and are parallel to the other two.

The pyramids  $mP$ , acuter or obtuser than the primary form, according as  $m >$  or  $< 1$ , have the same base as  $P$ ; and, like that form, have two sets of faces distinguished as  $+mP$  and  $-mP$ . The oblique rhombic prism on the same base as  $P$ , has the symbol  $\infty P$ .

The pyramids  $mPn$ ,  $[mPn]$  and the oblique prisms  $\infty Pn$ ,  $[\infty Pn]$  have rhombic bases differing in form from that of  $P$ .

The symbol  $[mP\infty]$  represents a series of clinodiagonal domes, that is to say, prisms whose faces and edges are parallel to the clinodiagonal.  $[P\infty]$  is the clino-

diagonal dome of the primary form: its four faces are similar, and its transverse sections are rhombuses similar to the orthodiagonal principal section, *caca* (fig. 283).

$mP\infty$  is the symbol of a series of orthodiagonal domes, acute or obtuse, according to the value of  $m$ . The four faces of such a dome are not all similar; two of them, which are opposite to the acute angles of the axial system, are distinguished as  $+mP\infty$ ; the other two, which are opposite to the obtuse angles of the axial system, as  $-mP\infty$ . Either of them may be present without the other.  $\pm P\infty$  is the orthodiagonal dome of the primary form; its transverse sections are similar to the clinodiagonal principal section.

$[\infty P\infty]$  represents the clinodiagonal end-faces, which cut the orthodiagonal and are parallel to the principal axis and clinodiagonal;  $\infty P\infty$ , the orthodiagonal end-faces, which cut the clinodiagonal and are parallel to the principal axis and orthodiagonal.

The following is a tabular view of the forms of the monoclinic system:

	( $m < 1$ )		( $m > 1$ )	
$\circ P\infty = \circ P$	$\pm mP\infty$	$\pm P\infty$	$\pm mP\infty$	$\infty P\infty$
$\circ Pn = \circ P$	$\pm mPn$	$\pm Pn$	$\pm mPn$	$\infty Pn$
$\circ P$	$\pm mP$	$\pm P$	$\pm mP$	$\infty P$
$[\circ Pn] = \circ P$	$\pm [mPn]$	$\pm [Pn]$	$\pm [mPn]$	$[\infty Pn]^*$
$[\circ P\infty] = \circ P$	$\pm [mP\infty]$	$\pm [P\infty]$	$\pm [mP\infty]$	

**Combinations.** The monoclinic system does not include any closed simple forms, every completely developed crystal belonging to it being a combination of dissimilar faces. Even the monoclinic pyramid,  $P$ , is a combination of two hemipyramids, each consisting of four faces similar to each other, but dissimilar to those of the other half.

In monoclinic, as in rhombic crystals, the following rule is of great use in determining the relative positions of the faces: *Any two faces which cut two of the axes at proportional distances from the centre, form a combination-edge parallel to the plane of those axes*; thus, two faces (such as  $a:2b:3c$ , or  $3P2$  and  $a:2b:5c$ , or  $5P2$ ) which cut the ortho- and clinodiagonal proportionally, intersect in an edge parallel to the basal section.

The combination of the basal end-face  $\circ P$  with the prism  $\infty P$  (fig. 284), so fre-

Fig. 284.

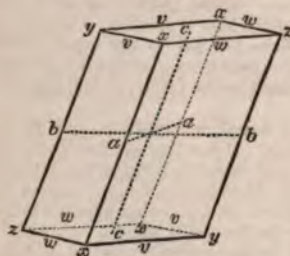


Fig. 285.



quently predominates in monoclinic crystals, that it may be conveniently taken as the starting point for the description of the rest. This combination is an oblique rhombic prism. The end-face  $\circ P$  is set symmetrically on the edges  $b$  situated in the clinodiagonal section, obliquely on the edges  $a$  in the orthodiagonal section. This combination may sometimes be easily mistaken for a rhombohedron, namely when the prismatic edges  $b$  are nearly equal to the combination-edges between  $\circ P$  and  $\infty P$ . Ferrous sulphate ( $\text{Fe}^2\text{SO}_4 + 7\text{H}_2\text{O}$ ), when part of the iron is replaced by another metal, as by copper, often takes the form represented in fig. 285, which, if the face  $+P\infty$  be removed, and the form of the crystal completed in the manner shown by the dotted lines, has very much the appearance of an acute rhombohedron, and has in fact actually been mistaken for one. In the rhombohedron, however, all the faces are similar, and the crystals cleave with equal facility parallel to either of them; but ferrous sulphate exhibits very distinct cleavage parallel to  $\circ P$ , and much less distinct parallel to  $\infty P$ . Moreover, the face  $\circ P$  makes with  $\infty P$  to the right in front, an angle of  $80^\circ 37'$ , and  $\infty P$  to the right in front makes with  $\infty P$  to the right behind, an angle of  $82^\circ 21'$ , whereas if the crystal were rhombohedral, these angles would be

\* Dana's symbols for the forms of the monoclinic system are the same as those for the rhombic system (see note page 145), excepting that an accent is placed over all numerals or letters referring to the clinodiagonal; thus  $mPn = mn\acute{n}$ ;  $[mPn] = m\acute{n}$ ;  $[mP\infty] = m\acute{\infty}$ ;  $[\infty P\infty] = \infty\acute{\infty}$ .

equal; and the face  $+P\infty$  is an isosceles triangle resting symmetrically on  $oP$  and obliquely on the two faces  $\infty P$ , whereas, in a rhombohedral crystal, the corresponding face  $oP$  of the hexagonal system would be an equilateral triangle resting symmetrically on all three faces.

The clinodiagonal edges  $b$  of the prism  $\infty P$  are symmetrically truncated by the orthodiagonal end-faces  $\infty P\infty$ , as in sugar (*fig. 286*). When this combination is developed at one end only of the orthodiagonal, it is not easily distinguished from the hemihedral combination  $\infty P \cdot \frac{P}{2}$  of the trimetric system, exhibited by sulphate of magnesium (*fig. 281*, p. 150), supposing this latter to be developed at one extremity only of the principal axis. The two faces  $\frac{P}{2}$  of *fig. 281* may then exhibit much the same character as the faces  $\infty P$  of the oblique rhombic prism (*fig. 286*), two faces  $\infty P$  of *fig. 281* being likewise situated like the basal end-faces  $oP$  of the oblique prism, and the other two like the orthodiagonal end-faces  $\infty P\infty$ . The two forms differ however in this respect, that the four faces  $\infty P$  of the rhombic prism are similar, whereas the faces  $oP$  of the monoclinic crystal are dissimilar to the faces  $\infty P\infty$ .

The orthodiagonal edges  $a$  of the prism  $\infty P$  are symmetrically truncated by the clinodiagonal end-faces [ $\infty P\infty$ ], as in ferrous sulphate (*fig. 287*), and in acetate of sodium (*fig. 291*).

Fig. 286.

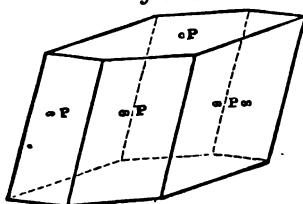


Fig. 287.

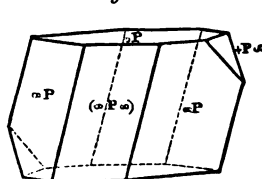


Fig. 288.

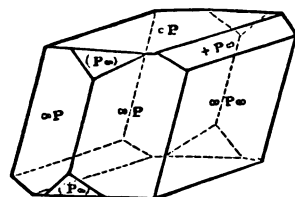
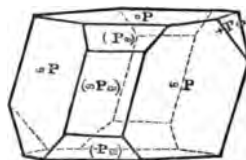


Fig. 289.



The combination-edges between  $oP$  and  $\infty P\infty$  (*fig. 286*) are of two kinds, two acute (the right above and left below) and two obtuse (the left above and right below). The former are truncated by the  $+P\infty$  faces, the latter by the  $-$  faces of the orthodiagonal dome  $\pm P\infty$ . *Fig. 288*, shows the acute edges truncated by  $+P\infty$ , a modification often occurring in sugar. The four combination-edges between  $oP$  and [ $\infty P\infty$ ] are similar, and are truncated by a clinodiagonal dome [ $P\infty$ ], as in ferrous sulphate (*fig. 289*).

The combination-edges between  $oP$  and  $\infty P$  (*fig. 284*) are of two kinds, four acute  $w$  (the two right above and the two left below) and four obtuse  $v$  (two left above and two right below). The former are truncated by the  $+P$  faces, the latter by the  $-$  faces of a pyramid  $\pm P$ , having the same base as the prism. *Fig. 290* shows the former in the combination  $\infty P \cdot oP \cdot +P$  of formate of copper; *fig. 291*, the latter in the combination  $\infty P \cdot oP \cdot [\infty P\infty] \cdot -P$  of acetate of sodium. The  $+$  and  $-$  faces of  $P$  may likewise occur together, as in the form of ferrous sulphate shown in *fig. 292*; but this is accidental, the occurrence of either set of faces being quite independent of that of the other.

The combination-summits between  $oP$  and  $\infty P$  (*fig. 284*) are of three kinds. Four of them,  $x$ , situated in the orthodiagonal principal section, are similar, and are truncated by the faces of a clinodiagonal dome [ $P\infty$ ], or more generally [ $mP\infty$ ], as in sugar (*fig. 288*), and in ferrous sulphate (*figs. 289, 292*). Of the other four combination-summits,  $y$ ,  $z$ , (situated in the clinodiagonal section), the two,  $z$ , which are opposite to the acute angles of the axes, are acute, and truncated by the  $+$  faces of an orthodiagonal dome  $+P\infty$ .



Fig. 290.

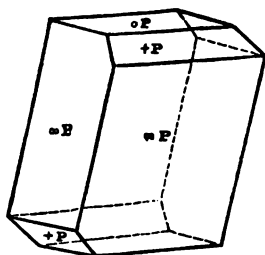
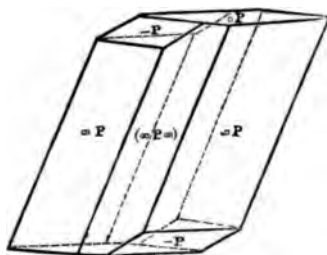


Fig. 291.



or  $+mP\infty$ , while the other two,  $y$ , opposite to the obtuse angles of the axes, are obtuse, and are truncated by the  $-$  faces of an orthodiagonal dome. Fig. 293 exhibits the former of these modifications, fig. 294 the latter, and fig. 292 both together. All these are forms of ferrous sulphate. When the  $+$  and  $-$  faces of the primary form  $P$  occur together, the terminal edges,  $C$  (fig. 283), between the principal axis and the orthodiagonal may be truncated by the clinodiagonal dome  $[P\infty]$ , with formation of parallel combination-edges, as in fig. 292. The terminal edges of  $P$  opposite the acute angles of the axes (the edges  $A$ , fig. 283) are truncated by  $+P\infty$ , with formation of parallel combination-edges; and those opposite to the obtuse angles of the axes ( $B$ , fig. 283) are replaced in like manner by  $-P\infty$ . Both these modifications are seen in fig. 292. The  $+$  and  $-$  faces of an acuter macrodiagonal dome replace these summits, with

Fig. 292.

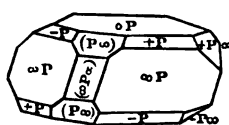


Fig. 293.

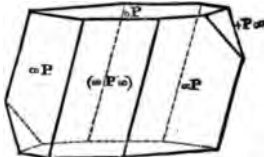


Fig. 294.

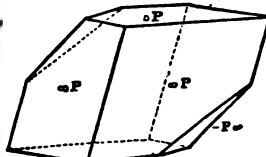


Fig. 295.

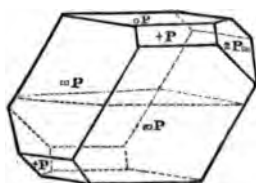


Fig. 296.

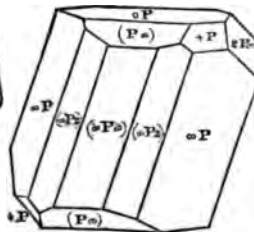


Fig. 297.

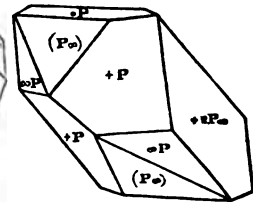


Fig. 298.

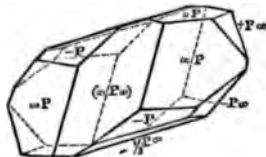
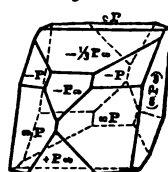


Fig. 299.



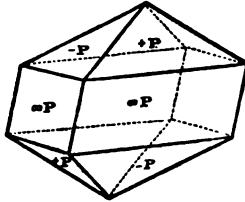
formation of combination-edges converging towards the extremities of the principal axis, as in acetate of copper (fig. 295) and in sulphate of nickel and potassium (figs. 296, 297). In figs. 298, 299, which represent the same combination of ferrous sulphate,  $\infty P \cdot [ \infty P\infty ] \cdot oP \cdot +P\infty \cdot -P\infty \cdot -P \cdot -\frac{1}{2} P\infty$  in two different positions, the face  $-P\infty$  is recognised by truncating the terminal edge between each pair of

—  $P$  faces, with parallel combination-edges. In the same figures, the faces of an obtuser dome —  $\frac{1}{2}P\infty$  included in the general formula —  $mP\infty$  (where  $m < 1$ ) may be recognised by forming with two contiguous —  $P$  faces, combination-edges which diverge towards the ends of the principal axis.

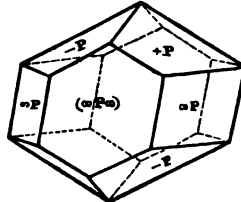
The orthodiagonal edges of  $\infty P$  are bevelled by the faces of a prism of different base [ $\infty Pn$ ] with longer clinodiagonal, as seen in *fig. 296*, where the beveling faces are [ $\infty P2$ ]; on the other hand, the clinodiagonal edges of  $\infty P$  are beveled by the faces of a prism  $\infty Pn$ , with longer orthodiagonal.

The ends of the prism  $\infty P$  are acuminated by the + and — faces of the pyramid  $P$  with equal base, as in gypsum (*fig. 300*). As the faces +  $P$  and —  $P$  are quite inde-

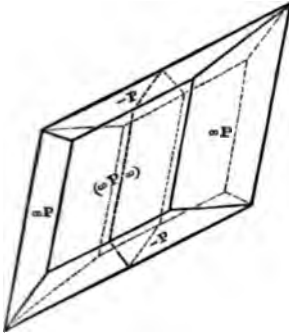
*Fig. 300.*



*Fig. 301.*



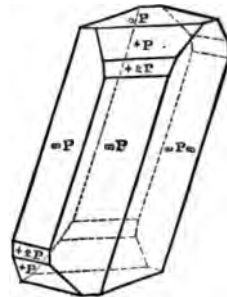
*Fig. 302.*



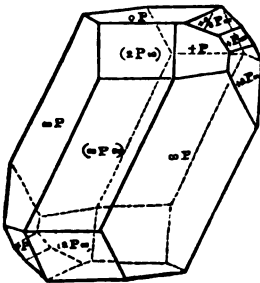
*Fig. 303.*



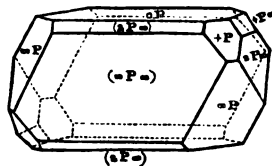
*Fig. 304.*



*Fig. 305.*



*Fig. 306.*



pendent of each other, one set may be quite subordinate or even absent, in which case the opposite set of faces form oblique bevelings at the ends of the prism, as in gypsum,  $\infty P \cdot -P$  [ $\infty P\infty$ ] (*fig. 302*), and augite,  $\infty P \cdot +P$  [ $\infty P\infty$ ] (*fig. 303*).

Faces of other pyramids likewise occur in monoclinic combinations, but generally of such as have the same base as the primary form, with a different principal axis; those, in short, which are included in the formula  $\pm mP$ ; thus borax exhibits the combination  $\infty P \cdot \infty P\infty \cdot \infty P + P \cdot + 2P$  (*fig. 304*).

The preceding details show that monoclinic combinations generally exhibit considerable analogy to those of the trimetric system; the chief difference between the two

is that in the former, hemipyramids and hemidomes occur, whereas in the latter the pyramids and domes are generally present with all their faces. A trimetric crystal properly placed, exhibits the same development in front as behind, and the same to the right as to the left; but a monoclinic crystal placed as described at page 151, though it exhibits the same development above backwards as above forwards, is differently developed to the right above and to the left above.

The choice of a principal axis is subject to the same uncertainty as in the trimetric system, arising from the circumstance that different crystals of the same substance may exhibit the greatest prismatic development in different directions. An instance of this is afforded by the two forms of feldspar represented in *figs.* 305, 306, the former being most elongated in the direction of the principal axis, the latter in that of the clinodiagonal.

The determination of monoclinic crystals is affected with a further source of uncertainty. In the case of a trimetric crystal, doubt may exist as to the choice of the principal axis, and as to the dimensions of the primary form, but not as to the quality of the several faces, *i. e.* whether they are pyramidal, prismatic, or terminal. But in a monoclinic crystal, any two similar faces may be regarded as terminal, or as forming a hemi-dome; any four similar faces as forming either a prism, or a clinodiagonal dome, or a hemipyramid; and in fact the same faces of a monoclinic crystal are often regarded in different lights by different observers, according to the particular varieties which have come under their notice. If gypsum occurred only in the form shown in *fig.* 302, the faces there marked  $-P$  might just as well be regarded as belonging to a clinodiagonal dome; but the occurrence of the variety of the same substance represented in *fig.* 301, renders the former view of these faces preferable. The only rule that can be given for these determinations is to choose the axes and assign the relations of the faces in the simplest possible manner, having regard to all the varieties of form that a substance presents.

Fig. 307.

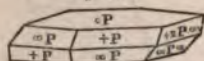


Fig. 308.

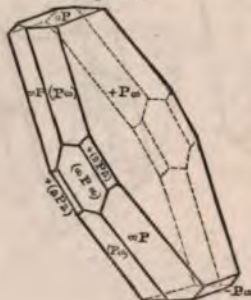


Fig. 310.

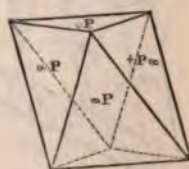
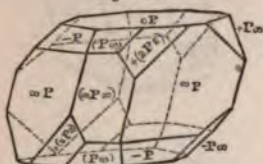


Fig. 309.



Monoclinic crystals present a prismatic, tabular, rhombohedral, or pyramidal character, according to the predominance of particular faces. The prismatic is the prevailing character, as may be seen from the instances already adduced. When the three conterminous edges of an oblique rhombic prism,  $\infty P \cdot oP$ , are nearly equal, the combination, as already observed, has very much the aspect of a rhombohedron, but may be distinguished therefrom by the inclinations of the faces, and by the character of its modifications (pp. 141, 152). The tabular character arises from the predominance of the terminal faces, as in acetate of zinc,  $oP \cdot \infty P \cdot +P \cdot +2P\infty \cdot \infty P\infty$  (*fig.* 307), where the predominant faces are  $oP$ , and in ferrous sulphate, *fig.* 308, where the tabular form arises from the predominance of  $+P\infty$ , as may be seen by comparing this form with *fig.* 309, which contains the same faces, but in different proportion.

A pyramidal character is often given to monoclinic crystals by the occurrence of one or more hemipyramids, as in gypsum (*fig.* 300). Another example is afforded by ferrous sulphate, which sometimes crystallises in the form shown in *fig.* 310, the same as *fig.* 285, but with the faces  $+P\infty$  more developed. Sulphate of nickel and potassium (*fig.* 296) also assumes the pyramidal form, *fig.* 297, by the enlargement of the faces  $+2P\infty$  and  $+P$ .

**Hemihedral Forms.** As the simple forms of the monoclinic system have at most but four faces, hemihedral forms are not of frequent occurrence. The most ordinary case is that in which the clinodiagonal dome  $[P\infty]$  is present with only half its faces. Thus, in sugar (*fig.* 288), the two front faces of this dome, are often present without the hinder ones. In ordinary tartaric acid also, two faces of  $[P\infty]$  (the front ones in a given position of the crystal) are present without the others, whereas in antitartaric acid



(i. 348), which differs from the ordinary acid only in possessing equal but opposite optical rotatory power, the *other* two faces of the same dome are present. Two crystals exhibiting this opposite hemihedral development are related to one another like an object and its reflected image, or, like the two hands, or the two halves of the face; they are similar but not superposable. This hemihedral relation is frequent in substances possessing the power of circular polarisation.

### Diclinic System.

*Diclinometric, Diclinohedral, Hemianorthic System.*—In this system, two of the axes are at right angles to each other, while the third (which may be regarded as the principal axis) is oblique to the other two. The occurrence of diclinic crystals has not yet been demonstrated with certainty, and as their simple forms and modes of combination are very similar to those of the following system, it is unnecessary to dwell upon them. The primary form is a symmetrical eight-sided pyramid, the basal section of which is a rhombus, and the other two principal sections rhomboids.

### Triclinic System.

*Triclinometric, Triclinohedral, Anorthic, Anorthotypic, Doubly oblique prismatic, Clinorhomboidal System* (Ein- und eingliedriges, Tetracdrisch-rhombisch-trimetrisches System).

Crystals of this system have three axes, all obliquely inclined to each other, and (in all actually observed forms) of unequal length. The axis in the direction of which the crystal is for the most part prismatically developed, is regarded as the principal axis ( $c$ ), the other two as secondary axes, the longer being called the macrodiagonal ( $b$ ), and the shorter the brachydiagonal ( $a$ ). In representing triclinic crystals, the secondary axes are supposed to lie in a horizontal plane, one or the other being drawn from left to right, accordingly as the peculiarities of the crystal may be most conveniently exhibited.

For the complete determination of a triclinic axial system, five magnitudes must be given, viz. the lengths of two of the axes referred to the third as unity, and the three acute angles which they form with each other; and for this determination, five independent measurements of the inclinations of planes are required.

The primary form in this system is a pyramid whose faces cut the three axes at the distances  $a$   $b$   $c$  from the centre. Fig. 311 exhibits such a pyramid, which may be regarded as the primary form of sulphate of copper ( $\text{Cu}^2\text{SO}_4 + 5\text{H}_2\text{O}$ ).  $a$   $a$  is the brachydiagonal,  $b$   $b$  the macrodiagonal,  $c$   $c$  the principal axis;  $a : b : c = 1.027 : 1.816 : 1$ . The acute angles of the axes are  $a : b = 77^\circ 37'$ ;  $b : c = 82^\circ 21'$ ;  $a : c = 73^\circ 10'$ .

The eight faces of this pyramid are of four kinds, only each pair of parallel faces being similar to each other, and each pair may occur in combinations quite independently of the rest. The six summits are of three kinds. The three principal sections, and indeed all sections parallel to any two of the axes are rhomboids. Of the twelve edges, only the parallel pairs are similar.

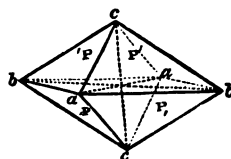
Of the four front faces of the pyramid, the right above is designated by  $P$ , the right below by  $P$ , the left above by  $P$ , the left below by  $P$ ; each of the back faces is designated by the same symbol as the front face to which it is parallel.

Other pyramids having the same base as the primary form are denoted by the general symbol  $mP$ , and those having different bases by  $mP_n$  and  $mP_n$ , just as in the trimetric system. Each of these pyramids has faces of four kinds, each pair of parallel faces being independent of the rest, and capable of occurring without them. The several faces of any individual pyramid are distinguished as to their position in the manner described for the primary form.

There are also triclinic prisms,  $\infty P$ , of the same base as the primary form; also prisms with different bases,  $\infty P_n$  and  $\infty P_n$ . Of the four faces of these prisms, only the parallel pairs are similar, and either pair may occur without the other. In the prism  $\infty P$  (for a position once determined), the right front face and the one behind parallel to it are denoted by  $\infty P$ , the other two by  $\infty P$ , and similarly for the other prisms.

Domes parallel to either of the secondary axes are denoted by the general symbols  $mP_\infty$  and  $mP_\infty$ ; in these also only the opposite faces are similar to each other; a pair of such faces occurring (for a given position of the crystal) in front above and at

Fig. 311.



the back below are denoted by the symbol  $m\bar{P}\infty$ , or  $m\bar{P}\infty$ ; in front below, and behind above, by  $mP\infty$ , or  $mP\infty$ ; to the right above and left below by  $mP'\infty$ , or  $mP'\infty$ ; to the left above and right below by  $m\bar{P}'\infty$ , or  $m\bar{P}'\infty$ .

Lastly, there are the basal end-faces  $\infty P$ , the macrodiagonal end-faces  $\infty P\infty$ , and the brachydiagonal end-faces  $\infty P'\infty$ , each pair of which cuts one of the axes and is parallel to the other two, as in the trimetric system.

All triclinic crystals are combinations made up of pairs of opposite faces of the simple forms. Each pair of parallel faces may be designated in various ways, either as end-faces, or as parallel faces of a prism, or of a pyramid. If, as frequently happens, three pairs of faces are predominant, as in *fig. 312*, the upper and under faces may be regarded as  $\infty P$ , the others as  $\infty P'$  and  $\infty P''$ , or as  $\infty P\infty$  and  $\infty P'\infty$ .

*Figs. 313, 314, 315* represent three forms of sulphate of copper, referred to the primary form represented in *fig. 311*.

*Fig. 313* consists of the primary form modified by the end-faces  $\infty P\infty$  and  $\infty P'\infty$ , and the hemiprisms  $\infty P'$  and  $\infty P''$ . If, however, only the  $P'$  faces of the primary pyramid are present (the top and bottom faces in the figure), and these faces, together with the faces parallel to the principal axis, are extended till they meet, the result is *fig. 314*, the most common form of sulphate of copper. Other faces likewise occur, though less developed. In determining the relations of these, and of tri-

Fig. 312.

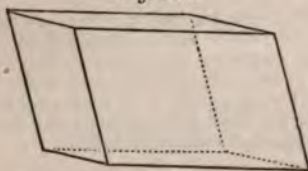


Fig. 313.



Fig. 314.



Fig. 315.



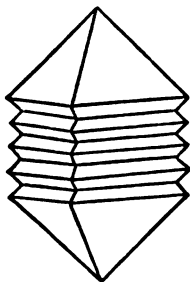
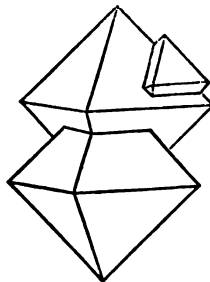
clinic combinations in general, the same rule holds good, as in the other systems, viz. that faces whose combination-edges are parallel to a principal section, cut the two axes contained in that section at proportional distances from the centre. In *fig. 315* the hemidomes  $2P'\infty$ ,  $P'\infty$ ,  $P'\infty$ ,  $2P'\infty$ , and the basic end-face  $\infty P$ , which are all parallel to the brachydiagonal, form with one another and with  $\infty P\infty$  combination-edges parallel to the basal principal section;  $\infty P$  forms with  $P'$  an edge parallel to that between  $P'$  and  $\infty P'$ . In *fig. 314*, the edges between  $P'$  and  $\infty P\infty$  are parallel to the macrodiagonal principal section; the faces which (in *fig. 315*) truncate these edges cut the principal axis and macrodiagonal in the same proportion as  $P'$ , that is to say, if they are also parallel to the brachydiagonal, they belong to the dome  $P'\infty$ . The face  $P'\infty$  is recognised by this character.  $2P'\infty$  truncates the (acute) edges between  $P'$  and  $\infty P$ . The edges between  $P'$  and  $\infty P\infty$  are parallel to the brachydiagonal principal section; in *fig. 315* they are partly truncated by the faces of a pyramid,  $2P'2$ , which cuts the principal axis and brachydiagonal in the same proportion as the primary form; instead of these faces, or together with them, are sometimes found the faces  $3P3$ .

The edges between the end-faces parallel to the principal axis and the adjacent prismatic faces are dissimilar, and either may be modified without the other. Thus, in sulphate of copper (*fig. 314*) the edges between  $\infty P\infty$  and  $\infty P'$  are often truncated by  $\infty P'2$ , while those between  $\infty P\infty$  and  $\infty P''$  remain unaltered; similarly, two faces of  $\infty P'2$  are often present alone, as truncations of the edges between  $\infty P\infty$  and  $\infty P'$ .

**Aggregations of Crystals.**

Crystals of the same substance are frequently united in groups, sometimes regularly, sometimes irregularly. Alum often forms groups of crystals regularly combined in the manner shown in *figs. 316, 317*, the octahedrons being united with their edges parallel to each other.

Aggregations of cubes end to end, so as to form elongated prisms, are also of frequent occurrence, as in chloride of potassium, which, under peculiar circumstances, has been seen to form thin silky threads, like tufts of cotton grass, made up of microscopic cubes (Warington, Chem. Soc. Qu. J. viii. 31). Chloride of sodium sometimes crystallises in such a manner that four such prismatic aggregates of cubes unite

*Fig. 316.**Fig. 317.*

together by their extremities, forming a hollow frame, and on this frame smaller ones similarly constituted are successively built up, till a four-sided pyramid is produced, composed wholly of little cubes; sometimes again it assumes the inverted position, like a funnel.

Groups of crystals (excepting when formed of cubes or prisms laid end to end) may always be distinguished from single crystals by presenting re-entering angles (*figs. 316, 317*). Sometimes, however, the re-entering angles are so shallow as not to be perceptible without the use of highly magnifying powers; the crystal then appears striated. Suppose, for example, the number of octahedrons united as in *fig. 316*, to be so much increased, and the distance between the horizontal parallel edges proportionately diminished, that the individual crystals can no longer be distinguished. The mass would then present the appearance of an octahedron having its horizontal edges replaced by prismatic faces, and these faces horizontally striated. Such striations, which are frequently observed on the faces of natural crystals, afford good indications of the internal structure of the crystal, and of the manner in which it has been formed by the juxtaposition of successive layers.

**Twin Crystals.**

When two crystals are regularly aggregated, but not according to the parallel mode of arrangement just described, they are called twins or macles; twins by contact, if the two individuals extend only to the plane of junction; twins by intersection, if each of them is continued beyond this plane and through the substance of the other. The plane of junction is always parallel to a face of the crystal either actual or possible, and one of the crystals is turned from its original position through an angle of  $180^\circ$ , round an axis perpendicular to the plane of junction.

The two crystals thus united are seldom fully developed, but for the most part only fragments of an ideal crystal; in many cases, each of them is the half of a completely developed crystal, and then the combination is called a hemitrope; such aggregates may be supposed to be produced by cutting a perfectly developed crystal in halves parallel to one of its faces, and turning one of the halves through an angle of  $180^\circ$ .

In the regular system, twin crystals of this kind are found bearing this relation to the regular octahedron, as shown in the annexed figures, where, if we suppose the octahedron (*fig. 318*) to be cut in two by the horizontal plane indicated by the dotted lines, and the upper fragment turned half round, the twin crystal (*fig. 319*) will be produced; examples of this arrangement are found in nitrate of lead, alum, magnetic iron ore, spinel, &c. Hemitropes also occur formed in like manner from the cube, regular dodecahedron, and tetrakis-hexahedron; an example of the last is found in native copper.

In most cases, twin-crystals thus formed may be distinguished from simple crystals



by the occurrence of re-entering angles; under peculiar circumstances, however, twins may be formed without reentering angles, as in some cases when each individual is smaller than the half of the ideally perfect crystal, or when the plane of junction is at right angles to the faces through which it passes, as in some cases of twin-formation from the regular dodecahedron. (See *Kopp's Krystallographie*, p. 87.)

Fig. 318.

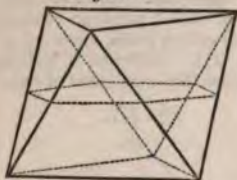
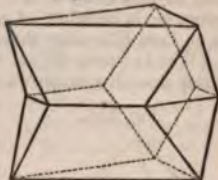


Fig. 319.



Intersecting twins are often formed from the cube (as in fluor-spar, galena, sal-ammoniac, chloride of potassium, &c.), the plane of junction (passing through the six reentering angles situated in one plane) being situated like the face of an octahedron (*fig. 320*). In these twins, and in all those which are derived from the holohedral forms of the regular system, the individual crystals are intergrown in such a manner that their axial systems are not parallel to one another; indeed, two holohedral

Fig. 320.

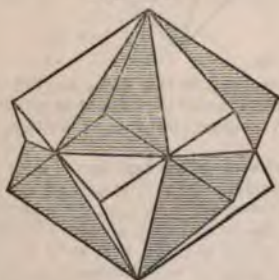
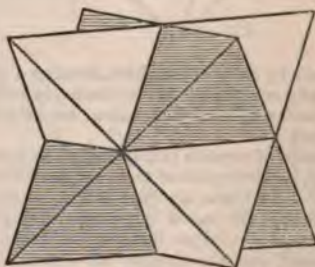


Fig. 321.

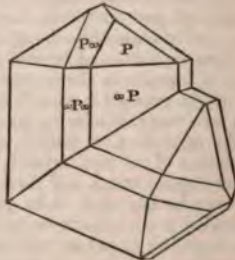


forms, so long as their axes remain parallel, can only unite so as to form aggregates like those represented in *figs. 316, 317*; as soon as they are brought together in such a manner as to have a common centre and parallel axes, they coincide altogether. But hemihedral crystals often form intersecting twins, with parallel system of axes, like the two tetrahedrons in *fig. 321*, because, though the axes are parallel, the faces may lie in opposite directions.

Fig. 322.



Fig. 323.



In the dimetric or quadratic system, twin-crystals occur both with parallel and non-parallel systems of axes. The former occur but rarely, and, as already explained, only in hemihedral forms. Intersecting twins, like *fig. 321*, are sometimes formed from quadratic spheroids,  $\pm \frac{P}{2}$ , as in copper pyrites. The same mineral also forms hemi-

tropic crystals, like *fig. 319*, derived from the quadratic pyramid  $+\frac{P}{2}$  and  $-\frac{P}{2}$  equally developed, which has the same shape as the regular octahedron.

But the most frequent twin-formation in the quadratic system is that formed by two crystals united by a face parallel to  $P\infty$ , one of them being turned half round. *Fig. 322* is a form of tin-stone,  $\infty P . P . \infty P\infty . P\infty$ . If this crystal be divided in the middle by a plane parallel to  $P\infty$ , and the lower half turned through an angle of  $180^\circ$ , the form represented in *fig. 323* will be produced.

Fig. 324.

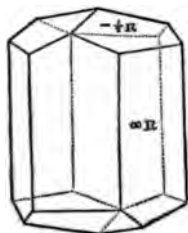
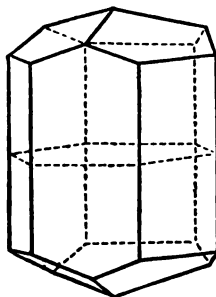


Fig. 325.



In the hexagonal system, intersecting twins are formed by two rhombohedrons penetrating each other like the cubes in *fig. 320*, and having the face  $\infty P$  in common; this form is exhibited by chabasite. Contact twins are exhibited by several forms of calcspar; thus, if we suppose the crystal represented in *fig. 324* to be cut through the middle by a horizontal plane, and the lower half turned half round, a hemitropic form will result, like that in *fig. 325*, which has the peculiarity of not exhibiting any re-entering angles. The scalenohedron (*fig. 326*), cut through the middle and turned half round, yields the form shown in *fig. 327*, which is often very regularly developed in calcspar.

Fig. 326.

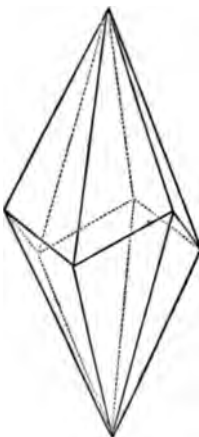
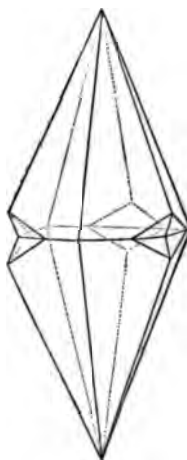


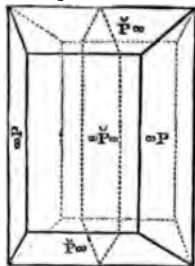
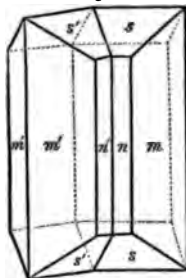
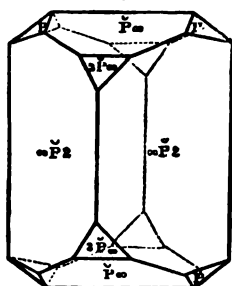
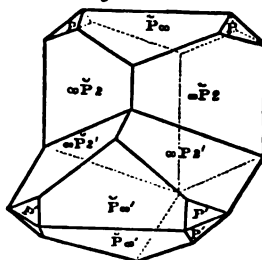
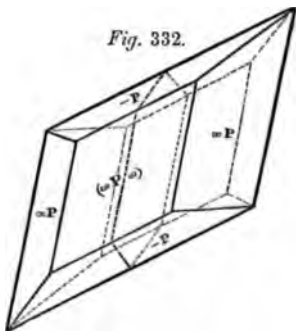
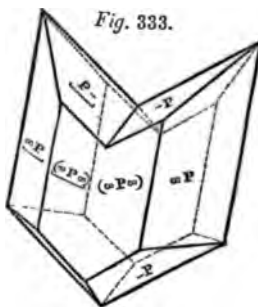
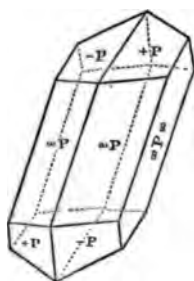
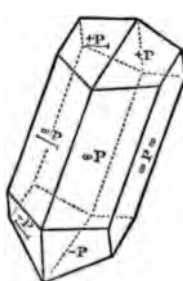
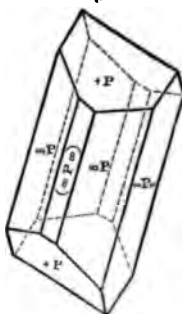
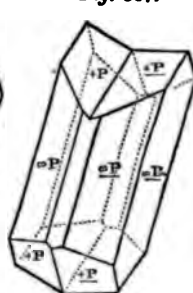
Fig. 327.



In the trimetric or rhombic system, twin crystals with parallel axial systems are of very rare occurrence. In those with non-parallel axes, the crystals are generally united by a face of the prism  $\infty P$ , or of the macrodiagonal dome  $P\infty$ , or of the brachydiagonal dome  $P\infty$ . *Fig. 328* shows the combination  $\infty P . \infty P\infty . P\infty$  occurring in arragonite. If we suppose this form cut in halves by a plane parallel to the left front face  $\infty P$ , and the left hand fragment turned through  $180^\circ$ , the hemitrope (*fig. 329*), which often occurs in arragonite, will be produced. The re-entering angle between the two front faces  $\infty P\infty$  is, however, frequently overgrown by the enlargement of the adjacent faces  $\infty P$ .

If we suppose the combination  $P . P\infty . \infty P2$ , occurring in sulphate of potassium (*fig. 330* without the face  $3P\infty$ ), to be halved parallel to the face  $P\infty$  in front below, and the lower half turned round  $180^\circ$ , the hemitrope, *fig. 331*, will result, which is a common form of sulphate of potassium.

In the monoclinic system, as hemihedral forms are very rare, nearly all the twin crystals which occur are such as have their axial systems not parallel. The contact face is almost always parallel to the orthodiagonal and one of the obliquely inclined axes, that is to say, either to the orthodiagonal end-faces  $\infty P\infty$ , or to the basic end-face  $\infty P$ . The twins are for the most part contact twins.

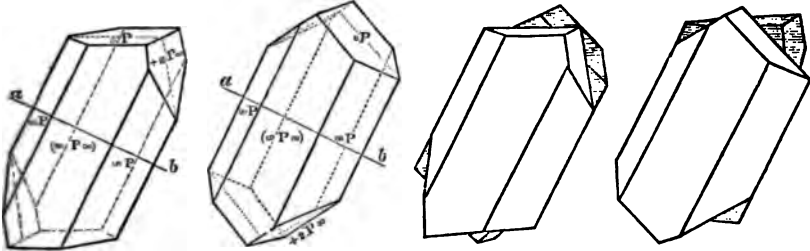
*Fig. 328.**Fig. 329.**Fig. 330.**Fig. 331.**Fig. 332.**Fig. 333.**Fig. 334.**Fig. 335.**Fig. 336.**Fig. 337.*

The twins whose contact-face is parallel to  $\infty P_{\infty}$  are often composed of individuals which appear like the halves of very regular crystals. If we imagine the forms represented by *fig. 332* (gypsum), *fig. 334* (ferricyanide of potassium), and *fig. 336* (augite),



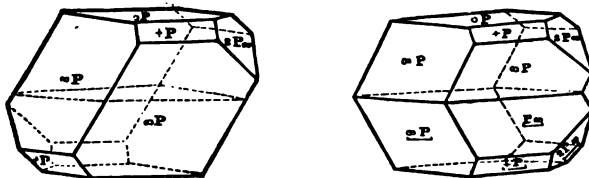
to be cut in halves by planes passing through the orthodiagonal and principal axis, and one half of the crystal turned through an angle of  $180^\circ$ , the first will produce *fig. 333*, the second, *fig. 335*, and the third, *fig. 337*, twin formations of frequent occurrence in the substances above mentioned.

In many instances, the two half-crystals composing a hemitrope formed in this manner, are not such as can be derived from the same, but belong to different crystals. An example of this mode of formation is presented by feldspar (orthoclase).

*Fig. 338.**Fig. 339.**Fig. 340.**Fig. 341.*

If the combination,  $\infty P. [\infty P\infty]. \infty P. + 2P\infty$  (*fig. 338*), exhibited by this mineral be supposed to revolve through  $180^\circ$  round a line  $ab$ , perpendicular to the orthodiagonal section, it will be brought into the position shown in *fig. 339*. These two crystals (which we will denote by  $p$  and  $q$ ) are, therefore, in the relative positions required for the formation of a twin crystal, according to the manner under consideration. But the mode in which they actually unite is this: Supposing each crystal to be cut in halves through the clinodiagonal section (as indicated by the dotted lines), the front half of  $p$  unites with the back half of  $q$ , producing *fig. 340*, and the back half of  $p$  with the front half of  $q$ , producing *fig. 341*. The two twin crystals thus produced are related to one another in form just like an object and its image reflected in a mirror.

In all the preceding twin formations of the monoclinic system, the principal axes of the individual crystal remain parallel, though the secondary axes do not. When, however, the contact-faces are parallel to the basal end-face  $oP$ , the principal axes of the two halves do not remain parallel; such a mode of union is exhibited by acetate of copper (*fig. 342*). If this crystal be cut in halves parallel to  $oP$ , and the lower

*Fig. 342.**Fig. 343.*

half turned round through  $180^\circ$ , the result is the hemitropic crystal shown in *fig. 343*. If the development of each crystalline fragment be continued beyond the contact plane, an intersection twin will result; such a mode of formation is exhibited by sphene.

In the triclinic system, twin crystals are of somewhat rare occurrence; an example is, however, afforded by triclinic feldspar (albite). The contact-face is in many cases parallel to  $\infty P\infty$  (corresponding to  $\infty P\infty$  in monoclinic feldspar), and then twins are produced resembling *figs. 340, 341*. In other cases, it is parallel to  $\infty P\infty$  (corresponding to  $[\infty P\infty]$  in monoclinic feldspar), and these last-mentioned twins exhibit the triclinic character very clearly. If a crystal of monoclinic feldspar be cut in halves through the clinodiagonal principal section, and one half turned round through  $180^\circ$ , the crystal still exhibits the same form as before; for the portions of the  $oP$  faces thus brought together fall into one plane, as also do the contiguous portions of the faces  $2P\infty$ . But if a crystal of triclinic feldspar (*fig. 344*), in which  $oP$  is oblique to  $\infty P\infty$ , be thus divided through the brachydiagonal section (as indicated by the dotted lines), and one half turned round through  $180^\circ$ , a hemitropic crystal (*fig. 345*) will be formed, in which one end (the upper end in the figure),  $oP$ , of the one half forms with  $oP$  of the other half, a re-entering angle of  $172^\circ 48'$ ; and  $P\infty$  forms with  $P\infty$  a re-

Fig. 344.

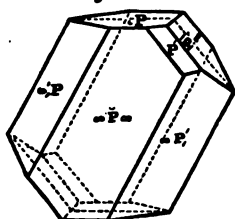
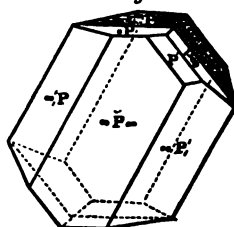


Fig. 345.



entering angle of  $175^{\circ} 12'$ , whilst at the other end, the corresponding faces are inclined to one another in projecting angles of the same magnitude.

Twins also occur in the triclinic system, in which the individuals are united by a face parallel to  $oP$ .

### Imperfect and Distorted Crystals.

Crystals are often imperfectly developed, or not bounded all round by crystalline faces, in consequence of being attached on the side to a matrix or to the surface of a vessel; and in very many cases they are distorted, that is to say, some of their similar faces are more developed than others, and may thus acquire even a different form. In all cases, however, their inclination to each other and to the axes remains unaltered. Every distorted crystal may be referred to a regular form, by supposing certain faces of the latter to approach nearer to the centre than the rest, or slices to be cut from the crystal parallel to certain faces.

Octahedral crystals of the regular system, such as alum, often exhibit only one complete octahedral face, the crystal having grown to the surface of the vessel by the

Fig. 346.

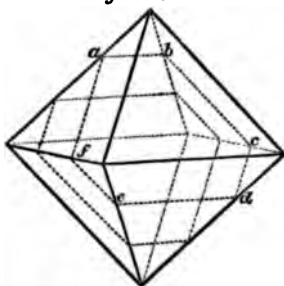


Fig. 347.

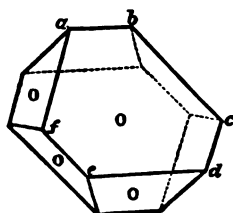


Fig. 348.

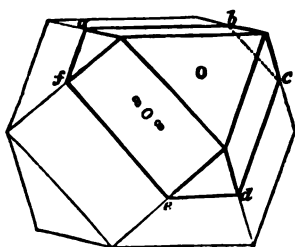
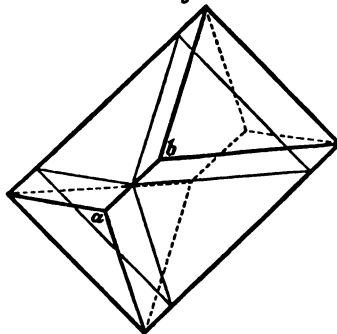


Fig. 349.



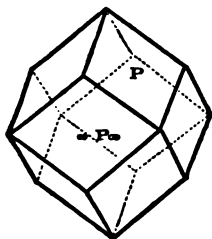
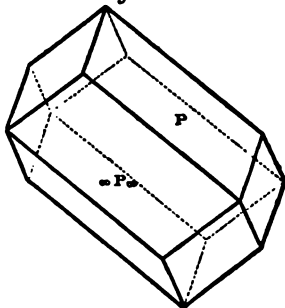
face  $a b c d e f$  (fig. 346), so that the portion below that plane has not been developed; sometimes only the middle of the crystal, shown in fig. 347, is developed, as if the octahedron (fig. 346) had been sliced parallel to the right front face  $O$ , as indicated by the

dotted lines. Nitrate of lead, which crystallises in the middle form between the cube and octahedron (*fig. 176*), often exhibits only portions of this form, like that bounded by the thick lines in *fig. 348*, the crystal having grown to the surface of the vessel by the plane  $a b c d e f$  parallel to  $O$ .

Cubic crystals are often reduced to square plates by being less developed in the direction of one axis than of the other two; sometimes again they are more or less elongated in the direction of one axis, as if a number of cubes had grown together by their faces, and thus acquire the appearance of elongated square prisms (*p. 169*).

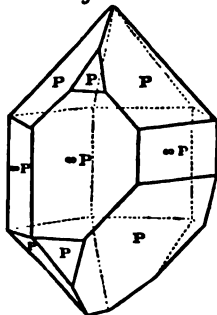
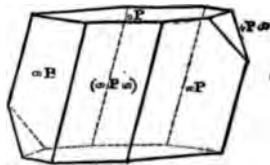
Octahedral crystals also are sometimes elongated in the direction of a line joining the middle points of two of their opposite faces, as shown in *fig. 349*, where the thin lines represent the ideal octahedron and the thick lines the distorted form. This distortion, which is seen in chrome-alum and nitrate of lead, gives the crystal the appearance of a rhombic prism bevelled at its extremities by the triangular faces resting perpendicularly on the acute edges of the prism, like *fig. 267*, *p. 147*.

Similar imperfections and distortions occur in crystals belonging to the other systems. A quadratic pyramid (*fig. 217*, *p. 133*) may be shortened or elongated in the same

*Fig. 350.**Fig. 351.*

manner as the regular octahedron, exhibiting forms like *figs. 347* and *349*. The combination of  $P$  and  $\infty P$  equally developed (*fig. 350*), which is the normal form of potassio-cupric chloride, often appears distorted in the manner shown in *fig. 351*, by elongation in the direction of a terminal edge of the pyramid, thereby acquiring the appearance of a hexagonal prism with trihedral summits.

Quartz, the normal form of which is a hexagonal prism with pyramidal summits  $P \cdot \infty P$  (*fig. 154*, *p. 117*), seldom or never exhibits this form in perfect regularity, some of the faces being more developed than others, as shown in *fig. 352*. Rhombohedrons also are often reduced to plates by shortening in one direction between two parallel faces, or elongated to prisms by abnormal development in the direction of one of the edges.

*Fig. 352.**Fig. 353.**Fig. 354.*

In the trimetric or rhombic system, the most common distortion arises from the unequal development of the four faces of a prism  $\infty P$ , two of them being larger and nearer to the centre than the rest, so that the transverse section, and the end-face in the combination  $\infty P \cdot \infty P$ , is altered from a rhombus to a rhomboid. The true character of the crystal, may, however, be recognised in such cases by the cleavage



and by the modifications. The crystal, if cleavable parallel to the prismatic faces, splits as easily in the direction of the smaller as of the larger of these faces. If an edge of the distorted prism is truncated, the truncation-face is equally inclined to the two adjacent faces,  $\infty P$ , and if its ends are beveled by domes, the faces of the domes are likewise equally inclined to the two prismatic faces.

Monoclinic crystals exhibit similar distortions; indeed the faces of an oblique rhombic prism are almost always unequally distant from the centre, so that the transverse section becomes a rhomboid instead of a rhombus. Crystals of ferrous sulphate of the normal form shown in *fig. 353* are often distorted in such a manner that two parallel faces  $\infty P$  and the basic end-faces  $oP$  are very much developed in one direction, producing the form shown in *fig. 354*; if the crystal is developed on one side only and attached on the other, the difficulty of recognising it is of course considerably increased.

*Curvature of Crystals.*—The surfaces of crystals are sometimes curved, in consequence of curvature in the laminae of which the crystal is made up. Crystals of diamond often have their faces curved to such an extent, as to make them appear almost like spheres. More frequently, a convex surface is opposite and parallel to a concave surface. This kind of distortion is seen in spathic iron, the crystals of which are sometimes saddle-shaped, in consequence of several curvatures occurring in the same face.

Fig. 355.

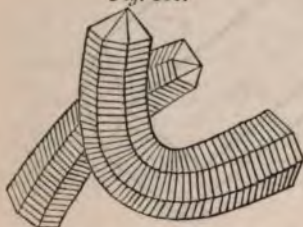
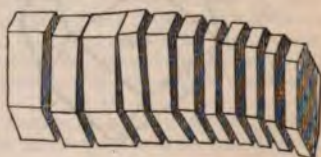


Fig. 356.



Another kind of curvature is seen in prismatic and aggregated crystals, and is especially frequent in such as are implanted or imbedded. *Fig. 355* exhibits this kind of distortion as seen in quartz. Six-sided prisms of calcite and prismatic crystals of gypsum are sometimes curved in a somewhat similar manner.

In many species, the crystals appear as if they had been broken transversely into several pieces, a slight displacement of which has given a curved form to the prism. This is common in tourmalin and beryl. The beryls of Monroe County, Connecticut, often present interrupted curvatures, as shown in *fig. 356*. (Dana.)

Most of the distortions above described occasion no change in the inclinations of the faces of crystals. But those imperfections which produce curved or striated faces necessarily lead to variations in the angles. The surfaces of large crystals often have a composite character, appearing, when examined by a magnifying glass, as if there had been a tendency to the formation of smaller crystals while the crystal was growing. Octahedrons of fluor-spar sometimes have their faces made up of little cubes. Such a cause produces more or less irregularity in the planes and their inclinations. Variations of form and angular magnitude also arise from the presence of foreign particles entangled in the crystallising mineral. Even the presence of foreign ingredients in solution when the crystallisation is going on, seems often to affect the angles, and such ingredients may be included in the crystal without being at all apparent, except on analysis. According to Baudrimont's measurements of calcspar, the rhombs of this mineral seldom have the three angles at their summits exactly equal.

The imperfections and distortions of crystals often present great obstacles to the determinations of crystalline forms, and even, as already observed, of the system to which a crystal belongs. In most cases, angular measurement may be safely relied on; but even this method, in consequence of the disturbing causes just noticed, may sometimes lead to erroneous results. In all cases, however, excepting in some of the grosser distortions, the character of the modifications affords an unerring guide to the system to which a crystal belongs, the general law which governs them being, that like parts of a crystal are similarly, unlike parts dissimilarly modified. This principle, already developed at some length in the descriptions of the several systems, may be further elucidated and facilitated in application by the following table taken from *Dana's Mineralogy*, i. 123.

Table of Modifications of Crystals.

1. All edges modified alike. 2. Angles truncated or replaced by 3 or 6 similar planes.		} MONOMETRIC System.	
1. All edges not modified alike. 2. Two* or some of the angles truncated or replaced by three or six similar planes.	Number of similar planes at extremities of crystal, 3 or some multiple of 3.	} HEXAGONAL System.	
	Number of similar planes at extremities of crystal neither 3 nor a multiple of 3.	The superior basal modifications in front not similar to the corresponding inferior in front or superior behind.	
		Two adjacent or two approximate simple planes impossible.	} TRICLINIC System.
		Two adjacent or two approximate simple planes possible.	
		MONOCLINIC System.	
		N. B. The right rhomboidal prism on its rhomboidal base may be distinguished from the other right prism by the dissimilar modifications of its lateral and basal edges and angles.	
		1. Similar planes at each base either four or eight in number.	
		2. All lateral† edges (if modified) similarly truncated or beveled.	
		} DIMETRIC System.	
		1. Similar planes at each base either two or four in number.	
		2. All lateral† edges (if modified) not similarly truncated or beveled.	
		} TRIMETRIC System.	

Important aids in the determination of the system to which a crystal belongs are also afforded:

a. By *cleavage*, which is similar parallel to like faces, dissimilar parallel to unlike faces.

b. By the *characters of surfaces*. Similar planes are alike in lustre, hardness, colour, striation, &c. If, for example, a cubic crystal has similar striae on all its six sides, it is monometric, but if the surfaces of one pair of its opposite sides differ from the rest, it belongs to some other system. Similar cleavage-faces also exhibit similar lustre, &c.

c. By the *optical relations* of the crystal. Monometric crystals refract light singly, but crystals of the dimetric and hexagonal systems have one axis of double refraction, and those belonging to the other systems have two axes of double refraction (p. 122). These characters are often of great use in determining the system to which a crystal belongs.

d. The *thermic relations* of crystals likewise differ according to the system to which they belong, as explained at page 122; so likewise do their relative elasticities in different directions; but the methods of observation on these points are too difficult of execution to be of much practical utility in the determination of crystals. (See HEAT.)

### Cleavage of Crystals.

Most crystals exhibit less coherence in some directions than in others, and consequently may be cloven or split in certain directions with more or less facility. Some crystals, as mica, may be split into laminae by the fingers; in others, a slight blow with a hammer is sufficient; others require the application of a sharp cutting instrument, and often considerable skill in its use. When other means fail, cleavage may sometimes be effected by heating the mineral and plunging it into cold water; this method sometimes succeeds with quartz. Many crystals cannot be cloven by any means: in these cases, however, the direction of cleavage is sometimes indicated by lines on the surface, or by cracks in the mass of the crystal. It is often important to observe these lines or cracks, even when cleavage is possible, in order to determine its direction before applying the knife.

The general laws with respect to cleavage are as follows:

1. Cleavage in crystals of the same species yields the same form and angles.
2. Cleavage takes place parallel either to one or more of the faces of a fundamental form, or to its diagonals, or to some of the secondary planes.

\* The rhombohedron is the only solid included in this division, any of whose angles admit of a truncation or replacement by three or six planes.

† The terminal edges of the octahedrons are here termed lateral, in order that the statements may be generally applicable to both prisms and octahedrons.



3. Cleavage is obtained with equal ease or difficulty parallel to *similar* faces, and with unequal ease or difficulty parallel to *dissimilar* faces.

4. Cleavage parallel to similar faces affords planes of similar lustre and appearance; in the contrary case, of dissimilar lustre and appearance.

Thus, cleavage is obtained with equal ease or difficulty parallel to all the faces of a cube, regular octahedron, rhombic dodecahedron, or rhombohedron, which are bounded by similar planes. The right square prism, right rhombic prism, and oblique rhombic prism ( $\infty P$ .  $\infty P$  of the dimetric, trimetric, and monoclinic systems respectively) cleave with equal ease or difficulty parallel to their lateral planes, since these also are similar. Frequently, however, these prisms cleave only parallel to their bases, and sometimes not even in this direction. In some cases, also, the cleavage is diagonal, in the square prism alike in both vertical planes, but unlike in the rhombic prisms. The right rectangular prism ( $\infty P\infty$ .  $\infty P\infty$ .  $\infty P$ , of the trimetric system), the right rhomboidal prism ( $\infty P\infty$ .  $\infty P\infty$ ],  $\infty P$  of the monoclinic system) and the oblique rhomboidal prism ( $\infty P'$ .  $\infty P'$ .  $\infty P$ , or  $\infty P$ .  $\infty P\infty$ .  $\infty P$ , of the triclinic system), have the cleavage unequal parallel to their faces, if attainable at all in these directions; moreover, cleavages in these two directions and parallel to the base yield faces of unlike lustre and general aspect. This is exemplified in gypsum, which in one direction cleaves with great facility into thin laminae of perfect transparency and highly polished surface; whilst in a second direction, the laminae first bend and then break, exhibiting a surface which is not smooth or possessed of much lustre; and in a third direction, the laminae are brittle, break immediately on attempting to bend them, and exhibit a surface smoother than the second, but not polished. In thick masses, the second and third cleavages are scarcely attainable. Two of these cleavages incline at an oblique angle, but one is at right angles to the third, showing that the crystal is monoclinic.

#### Measurement of Crystals.

A crystal is determined when we know the relative lengths of the axes for each of the primary forms which compose it, and their inclination, in case they are not at right angles to each other. These magnitudes cannot however be measured directly; the only element of the form admitting of direct measurement is the inclination of the faces one to another; and as these inclinations are connected with the ratios and inclinations of the axes by fixed geometrical relations, the latter may be determined by calculation, when a sufficient number of the dihedral angles of the crystal have been measured. The number of angular measurements absolutely required for each form is of course equal to the number of unknown quantities to be determined; thus for a square pyramid  $a:b:c$  (p. 133), the only magnitude to be determined is the ratio  $\frac{a}{c}$ ; and for this, one angular measurement will suffice, viz. the angle either in the

terminal or in the lateral edges. For a rhombic pyramid  $a:b:c$ , two quantities have to be determined, viz. the lengths of two of the axes referred to the third as unity, and for this, two independent measurements are required. For a monoclinic pyramid, in which, in addition to the two ratios just mentioned, the inclination of the principal axis to the clinodiagonal has to be determined, three independent angular measurements are required. In all cases, however, it is advisable to take as many angular measurements as possible, in order to check the values first determined.

For the formulæ which express the relations between the inclinations of faces and the ratios and inclinations of the axes in the several systems, we must refer to more detailed works\*, and confine ourselves here to the description of the instruments used for measuring the angles of crystals. These instruments are called GONIOMETERS, and are of two kinds, the *Application- or Hand-goniometer*, and the *Reflecting Goniometer*.

The hand-goniometer is a divided semicircle  $abd$  (fig. 357), to which are adapted two metal rules, one  $km$  being fixed, the other  $gh$  movable round a pin  $c$  at the centre of the semicircle. Both these rules have slits, so that they may be moved backwards and forwards, making the sides of the angle  $knh$  longer or shorter as may be required. A straight line drawn through the point  $c$  and the middle of the rule  $km$  passes through the points  $0^\circ$  and  $180^\circ$  of the divided semicircle. The other rule,  $gh$ , is narrower in the part which moves round the semicircle (and likewise bevelled), so that the edge  $gi$  produced would pass through the centre  $c$ . The angle which the edge  $gi$  marks on the graduated arc, is therefore equal to the angle  $n$  contained between the edges  $kn$ ,  $nh$ .

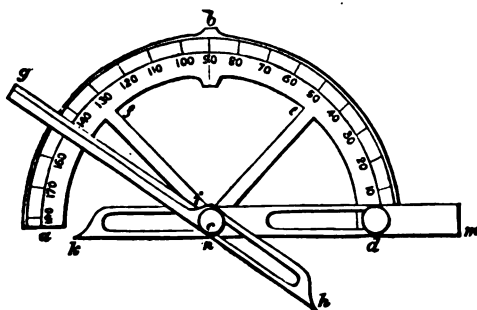
The crystal to be measured is placed between the rules  $kn$ ,  $nh$  in such a manner

\* Dana, *System of Mineralogy*, vol. i. 8vo. New York, 1858. Miller, *Treatise on Crystallography*, vol. i. 8vo. Cambridge, 1839. Brooke and Miller, new edition of Phillips's *Mineralogy*, 12mo. London, 1852. Kopp, *Einleitung in die Krystallographie*, 8vo. Braunschweig, 1847.



that the edges of these rules may both be at right angles to the line of intersection of the two faces whose inclination is to be measured. The edge  $k n$  is applied close to one face of the crystal, and the other rule  $g h$  is moved round  $c$ , till the edge  $n h$  coincides exactly with the other face. The inclination is then indicated by the number of degrees in the arc  $d e g$ .

Fig. 357.



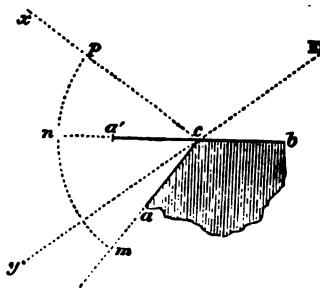
If one of the faces of the crystal presents irregularities arising from small crystals being implanted on it, the edge  $k n$  must be laid closely on the smooth face, and the other edge  $n h$ , brought as close as possible to the other face and parallel to it.

In measuring crystals implanted on a surface, the parts  $k n$ ,  $h n$  of the rules must be moved along the slits into the required positions. In such cases, the part  $a b$  of the graduated arc is often in the way. To obviate this inconvenience, the semicircle is in some instruments cut through at  $b$  and the two parts joined by a hinge: there is then also a strip of metal  $f i$  movable about  $c$ , which, when placed in the position shown in the figure, serves to keep the two halves of the semicircle in the same plane, but when moved towards  $e$ , allows the half  $a b$  to be turned round to the back of  $b d$ .

This instrument is very convenient, and indeed indispensable, for measuring the angles of large crystals; on the other hand, it is evidently inapplicable to small crystals or to such as are very soft or friable; and as small crystals are of much more frequent occurrence than larger ones, and generally exhibit the best defined forms and flattest surfaces, the use of the hand-goniometer is necessarily somewhat limited. For these reasons, the reflecting goniometer of Wollaston, which also gives greater accuracy of measurement, is much more frequently used.

The reflecting goniometer depends upon the following principle. Let  $bac$  (Fig. 358) be a section of a crystal, the angle  $c$  of which is to be measured. The crystal is supposed to be fixed so that its edge is exactly in the prolongation of the axis of a divided circle  $m n p$ . Let a mark  $y$  (a black line drawn on paper for example), be so fixed that the eye of the observer placed at  $E$  may see this mark  $y$  directly, in the same direction as the image of an object  $x$  above the crystal, reflected from the bright surface  $bc$ . Now suppose the crystal to be turned round the edge  $c$  till the face  $ca$  comes into the position  $ca'$ , in the prolongation of  $bc$ ; the eye placed at  $E$  will still see the image of  $x$  in the same direction  $E y$ , by reflection from  $ca'$ . But it is evident that the angle  $a c a'$  (measured by the arc  $m n$ ) through which the crystal has been turned, is the supplement of  $b c a$ , the angle to be measured: hence the following rule: The angle  $a$ , contained between two faces of a crystal, is the supplement of the angle through which the crystal must be turned, in order that these two faces may reflect the image of a given object in the same direction: or if this latter angle is  $= a$ , the angle between the two faces of the crystal will be  $180^\circ - a$ .

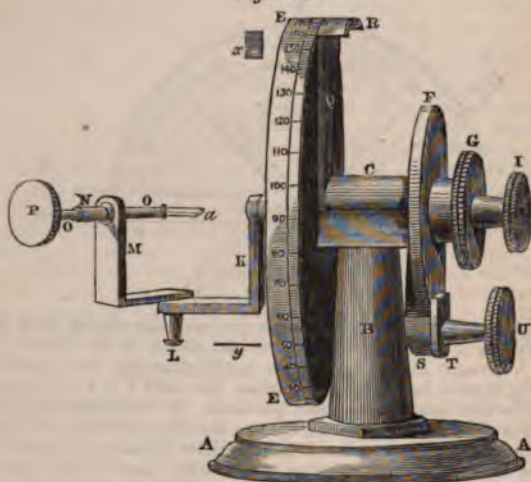
Fig. 358.



The instrument by which this principle is applied to the measurement of crystals is represented in *fig. 359*. It consists of a vertical circle  $E E$ , divided on the edge, and turning upon a horizontal axis passing through the socket  $C$ , which is fixed upon the pillar  $B$ , supported on a heavy foot  $A$ . This axis likewise carries a smooth-edged disc

F, and a mill-edged disc G, both immovably fixed to it. The disc G is for turning the graduated circle round; the use of the disc F is to assist in clamping it, which is effected by compressing the lower edge of F between two plates of metal S, T, the former attached to the socket C, by means of the screw U. A vernier R, attached by the metal strap Q to the socket C, serves to read off the degrees on the circle E E. The axis which carries this circle and the discs F, G, is hollow, and encloses a thinner

Fig. 359.



axis which turns within it somewhat stiffly, and carries at one end the mill-edged disc I, and at the other a bent brass rod K. This rod carries a socket L in which another bent rod M turns, and in this is another socket N, through which passes a rod O O, which can be moved backwards and forwards, and turned round by the disc P; at the other end of this rod the crystal to be measured is fastened with wax.

To use the instrument, it is placed in front of a window with the plane of the circle E vertical, and at right angles to the plane of the window, the axes being then parallel to the horizontal bars of the window, one of which—or better, a slit in a piece of black paper fastened to one of the panes, may serve for the object *x*—to be reflected from the planes of the crystal. The observer, standing in front of the instrument, may bring his eye into such a position above the crystal, as to see a horizontal black line *y* drawn below the window, just along the edge of the crystal; and by turning the crystal round by the disc P, he may bring one face of it into such a position that the reflected image of the window-bar *x* may just coincide with the line *y* seen directly. It is, however, absolutely necessary that the edge of the crystal be brought exactly into a line with the axis of the instrument. This must first be done as nearly as possible by the unassisted eye: but to obtain a more exact adjustment, the crystal must be turned, by means of the movements at L and N, till the reflected image of the window-bar seen from each face of the crystal, is parallel to the line *y*, that is to say, horizontal. The crystal is then properly placed. To measure the angle, the disc G is turned round till 180° on the divided circle E E coincides with the zero of the vernier; the screw U is tightened so as to clamp the circle E E; and the crystal is turned round by the disc I, till the image of *x* from one face coincides with the line *y*. The circle is then unclamped, and turned round by the disc G, till the other face of the crystal is brought into the same position. The division of the circle which is thus brought opposite to the zero of the vernier, gives directly the number of degrees in the angle contained between the two faces of the crystal. (For other forms of the reflecting goniometer, see *Dana's Mineralogy*, i. 127.)

When the faces of a crystal are bright and reflect well, a comparatively distant object, such as the edge of the roof of an opposite house, may be viewed in them, and the angles may then be measured within a few minutes; the greater the distance of this object, the more exact, *ceteris paribus*, will be the measurement. With crystals of less reflecting power, nearer objects, such as the window-bars, must be chosen; sometimes indeed it is necessary to use the flame of a candle placed behind a screen having a horizontal slit. Crystals whose surfaces have little or no reflecting power may sometimes be measured with the reflecting goniometer, by attaching to their faces very thin

plates of mica, by means of water or oil of turpentine, according to the nature of the crystal.

Artificial crystals generally lose their lustre when touched with the hand, and will not bear cleaning. The best way of manipulating with them, is to fasten them with wax by their duller surface to a little piece of wood, which may then be used as a handle, and for attaching them to the goniometer.

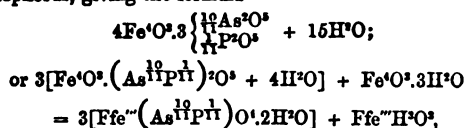
It is important to observe that the angles of crystals often change to a certain extent with change of temperature; hence, for accurate measurements, the temperature should always be noted.

**CUBAN.** A native sulphide of iron and copper,  $\text{Cu}^2\text{Fe}^2\text{S}^3$  (see page 79).

**CUBE ORE.** *Pharmacosiderite, Siderite, Würfelerz.* A variety of native arsenate of copper occurring in crystals of the regular system, viz. cubes, sometimes perfect, sometimes having their edges or angles truncated, e.g.  $\infty 00 \cdot \infty 0$  (fig. 195),  $\infty 00 \cdot \frac{0}{2}$  (fig. 198), and others. Cleavage cubic, imperfect. The cube-faces are sometimes striated parallel to their intersections with the octahedral faces. Planes often curved. Rarely granular. Specific gravity = 2.9 to 3. Hardness = 2.5. Lustre adamantine, not very distinct. Colour olive-green to blackish-brown, also passing into grass-green and emerald-green. Streak olive-green to brown, yellow, pale. Subtranslucent. Rather sectile. Pyroelectric. (Dana, ii. 422.)

When heated, it gives off water and turns red. Before the blowpipe on charcoal, it gives off arsenic vapours, and melts in the reducing flame to a grey shining slag, which gives with fluxes the reactions of iron and arsenic. Soluble in hydrochloric acid. Caustic potash quickly turns it reddish-brown, and decomposes it for the most part.

An analysis by Berzelius gave 40.92 per cent.  $\text{As}^2\text{O}^3$ , 2.57  $\text{P}^2\text{O}^5$ , 39.90  $\text{Fe}^2\text{O}^3$ , 0.66  $\text{Cu}^2\text{O}$ , and 18.94 water (= 102.99; after deduction of 1.76 per cent. matrix). If the small quantity of copper be regarded as  $\text{Cu}^2\text{AsO}^4$  and deducted, the remainder may be regarded as a tetrabasic ferric arsenate with 15 at. water, in which  $\frac{1}{10}$  of the arsenic is replaced by phosphorus, giving the formula —



in which the first member has the form of Scorodite. (Ram m. Mineralch. p. 372.)

Cube-ore was formerly obtained from certain mines in Cornwall, where it occurred coating cavities in quartz, with ores of copper. It is now found in small shining crystals at Bundle Gill, Cumberland; also in Australia; at St. Leonard in France, and at Schneeberg and Schwarzenberg, in Saxony.

**CUBBERA CLUSII MIQ.** The fruit of the black pepper of West Africa, called *Piper caudatum*. According to Stenhouse (Ann. Ch. Pharm. xcv. 106), it contains piperin and not cubebin, so that it must be regarded as pepper, not as cubebs.

**CUBBERINE.** An isomeric modification of oil of cubebs (p. 172).

**CUBEBIN.**  $\text{C}^{11}\text{H}^{10}\text{O}^2$ ? (Soubeiran and Capitaine, Ann. Ch. Pharm. xxxi. 190. Riegel, N. Jahrb. Pharm. viii. 96. Schuck, N. Repert. Pharm. i. 213.) A crystalline substance existing in cubebs. It is obtained by exhausting with alcohol the pulpy residue left after the preparation of the essential oil of cubebs, treating the alcoholic solution with potash, washing the resulting precipitate with water, and crystallising from alcohol (Soubeiran and Capitaine).—Schuck prepares cubebin by mixing cubebene with  $\frac{1}{2}$  of its weight of quicklime, exhausting with alcohol, treating the evaporated extract with dilute potash, dissolving the residue in alcohol, decolorising with animal charcoal, and leaving the solution to crystallise. 17 oz. of cubebene thus treated yielded 15 grains of cubebin.

Cubebin crystallises in groups of small white needles. It is tasteless, inodorous, melts at  $120^\circ\text{C}$ . (Schuck), but cannot be volatilised without decomposition. It is very slightly soluble in water and in cold alcohol, more soluble in boiling alcohol, the solution solidifying to a pulp on cooling. Ether dissolves 3.75 per cent. cubebin at  $12^\circ\text{C}$ ., and more when heated. Cubebin also dissolves in acetic acid, and in oils both fixed and volatile. Strong sulphuric acid first colours it of a fine bright red, very much like that which it imparts to salicin, but afterwards changing to crimson.

**CUBEBS.** The fruit of *Piper Cubeba*, L., a native of Java. When dry, it forms roundish blackish-grey berries of the size of pepper, enclosing a hard white oily seed. It has an aromatic peppery odour, and a sharp bitter taste. According to Monheim (J. Chim. méd. xi. 352), it contains 2.5 per cent. green volatile oil, 1.1 yellow liquid



## 172 CUBEBS, CAMPHOR OF—CULILABAN, OIL OF.

oil, 6.0 cubebin, 1.5 balsamic resin, 3.0 waxy matter, 6.0 extractive matter, 1.5 chloride of sodium, and 64.0 woody fibre.

**CUBEBS, CAMPHOR OF.** (Blanchet and Sell, Ann. Ch. Pharm. vi. 294.) *Stearoptene of Oil of Cubebs.* The volatile oil of cubebs, after rectification with water, deposits this compound in rhombic crystals P. oP.  $\infty$ P, in which P : P in the terminal edges =  $115^{\circ} 40'$  and  $75^{\circ} 24'$ , and in the lateral edges =  $145^{\circ}$ . Cleavage perfect, parallel to oP. It melts at  $68^{\circ}$  C., boils at  $150^{\circ}$ , and distils without alteration. It is insoluble in water, soluble in alcohol, ether, and volatile oils. The alcoholic solution possesses optical rotatory power.

According to Blanchet and Sell's analyses, the camphor contains from 80.1 to 81.1 per cent. carbon, and 11.1 to 11.7 hydrogen, agreeing approximately with the formula  $C^{13}H^{20}O$  or  $C^{13}H^{21},H^{20}O$ , whence it appears to be a hydrate of oil of cubebs or of cubebene.

The camphor dissolves in strong sulphuric acid, forming apparently a conjugated acid. It is partially soluble in boiling potash. By nitric acid it is converted into a brown resin; by chlorine into a viscid substance.

**CUBEBS, OIL OF.**  $C^{13}H^{21}$ . (Müller, Ann. Ch. Pharm. ii. 90. Blanchet and Sell, *ibid.* vi. 294. Winckler, *ibid.* viii. 203. Soubeiran and Capitaine, *ibid.* xxxiv. 311. Aubergier, Rev. scient. iv. 220. Brooke, Annals of Philosophy, new series, v. 450. Gerh. iii. 634.) This oil is obtained by distilling cubebs with water. It is colourless, viscid, of specific gravity 0.929, has an aromatic odour, and a camphor-like spicy taste. It boils between  $250^{\circ}$  and  $260^{\circ}$  C., always, however, with partial decomposition. Exposed to the air, it becomes thicker and resinous. It turns the plane of polarisation of a luminous ray to the left.

*Hydrochlorate of oil of cubebs*,  $C^{13}H^{21},2HCl$ , is produced by passing hydrochloric acid gas into the rectified oil. It forms oblique prisms, colourless, tasteless, inodorous, melting at  $131^{\circ}$  C., very soluble in alcohol. They turn the plane of polarisation to the left.

*Cubebene.*—Oil of cubebs distilled with sulphuric acid is converted into an isomeric oil, cubebene, possessing much less optical rotatory power than the original oil.

**CUBICITE.** Syn. with ANALCIME (i. 210).

**CUBILOSE.** A constituent of the edible birds' nests of India, exhibiting the general properties of the neutral albuminoids. (Payen, Compt. rend. xlix. 528.)

**CUBOICITE.** Syn. with CHARASITE.

**CUBOITE.** Syn. with ANALCIME, also with SODALITE.

**CUCUMIS.** A genus of cucurbitaceous plants, including the cucumber, melon, and some kinds of gourd.

The fruit of *Cucumis colocynthis*, the bitter apple, or colocynth gourd, contains a pulp or pith which, when separated from the seeds, constitutes the purgative drug colocynth. (See COLOCYNTHIN, p. 78.)

*C. melo*, the melon, has been examined by Payen (Buchn. Repert. lxxvi. 104): it contains the usual vegetable constituents. The root contains, according to Torosiewicz (*ibid.* xlv. 1), an emetic principle, melonemetin; and yields 6.4 per cent. of ash, of which 5 per cent. consists of salts soluble in water, and 95 per cent. insoluble matter.

The fruit of *C. prophetarum* contains, according to Winckler, a bitter principle, which, according to Walz, is essentially a resin (*Prophetinharz*), containing  $C^{22}H^{32}O^8$ , separable into *propheterin* or *prophetein*,  $C^{20}H^{30}O^4$ , and a carbohydrate (glucose).

**CUCURBITA.** Another genus of cucurbitaceous plants, including the common gourd, *C. maxima*, with its numerous varieties, the vegetable marrow, *C. ovifera*, the orange gourd, *C. aurantia*, the squash or bush gourd, *C. melopepo*, the bottle gourd, *C. lagenaria*, &c. &c. Most of them are eatable; but the orange gourd is bitter, and the bottle gourd is a dangerous poison. The fruit of this last-mentioned species, however, contains, according to Marquardt (J. pr. Chem. xi. 500), about 6 per cent. of sugar, and is used in Hungary for the extraction of sugar. The seeds contain a mild fixed oil.—The water-melon, *C. citrullus*, has been examined by Landerer (Buchn. Repert. lxxvi. 104). Lenoir (J. Pharm. [3] xx. 356) found in it 3 per cent. sugar, 30 per cent. residue, and 67 water.

**CUDBEAR.** See ARCHIL (i. 355).

**CULEBRITE.** A name sometimes given to a mineral from Culebras in Mexico, resembling Riolite, and said to consist of selenide of zinc and sulphide of mercury. (Handw. d. Chem. ii. [3] 235.)

**CULILABAN or CULILAWAN, OIL OF.** A volatile oil obtained from the bark of *Laurus Culilaban* or *Culilawan*, or *Cinnamomum Culilawan* (Nees), a native of the Moluccas, by distillation with water. It is colourless; smells like oil of cajeput

and oil of cloves; is heavier than water; dissolves, with red colour, in nitric acid, forming a solution from which water throws down a brick-red resin (Schloss). Heated with 6 parts of fuming nitric acid, it swells up strongly, gives off nitrous gas, and, when repeatedly distilled, yields oxalic acid, amounting to  $\frac{1}{3}$  of the oil. (Gm. xvi. 364.)

**CUMENE.** *Cumol. Hydride of Cumenyl.*  $C^8H^{12} = C^8H^{11}.H$ . (Pelletier and Walter [1837], Ann. Ch. Phys. [2] lxvii. 99. Gerhardt and Cahours, Ann. Ch. Phys. [3] i. 87, 372; Ann. Ch. Pharm. xxxviii. 88. Gerhardt, Ann. Ch. Phys. [3] xiv. 107. Abel, Ann. Ch. Pharm. lxiii. 308; Mem. Chem. Soc. iii. 441; Phil. Mag. xxxii. 63. Cahours, Compt. rend. xxiv. 557, xxx. 321. Mansfield, Chem. Soc. Qu. J. i. 244; Ann. Ch. Pharm. lxix. 179. Gerhardt and Liës-Bodart, Compt. rend. xxix. 506; Compt. chim. 1849, 385; Ann. Ch. Pharm. lxxii. 293. Ritthausen, J. pr. Chem. lxi. 79. Church, Phil. Mag. [4] ix. 256. Liës-Bodart, Compt. rend. xliii. 394; Ann. Ch. Pharm. 100, 352. Warren de la Rue and H. Müller, Chem. Gaz. 1856, 375; J. pr. Chem. lxx. 30.

This body, discovered by Gerhardt and Cahours in 1840, is probably identical with the resin-oil or retinyl obtained by Pelletier and Walter from the resin of *Pinus maritima* (see *Pinus-resins*), and probably also with the hydrocarbon produced by the action of phosphoric anhydride on phorone. It is isomeric with mesitylene, with methol, and with a hydrocarbon discovered by Church among the products of the distillation of eugenate of barium.

Cumene exists ready formed in Burmese naphtha, that substance, when aqueous vapour at 200° C. is passed through it, yielding hydrocarbons from which sulpho-cumenic acid is produced by the action of oil of vitriol (Warren de la Rue and H. Müller). It is produced: 1. In the distillation of cuminic acid with excess of baryta (Gerhardt and Cahours).—2. In the dry distillation of the resin of *Pinus maritima* (Pelletier and Walter); of the wood of that tree, passing over into the crude spirit (Cahours); and of coal, being found in coal-tar naphtha (Mansfield, Ritthausen, Church).—3. In the distillation of phorone with anhydrous phosphoric acid. (Gerhardt and Liës; Liës.)

**Preparation.**—1. *From Cuminic Acid.*—1 pt. of cuminic acid is gradually heated in a retort with 4 pts. of baryta. When the heat is carefully applied, and not more than 6 grammes of cuminic acid are used, nothing but colourless cumene passes over, while carbonate of barium remains behind. The use of larger quantities at once is not to be recommended (Gerhardt and Cahours). Abel mixes cuminic acid with 4 pts. of lime, and heats the mixture nearly to redness in a copper retort placed in a deep sand-bath. The colourless distillate has an unpleasant empyreumatic odour, which it retains even after rectification over hydrate of potassium. Abel therefore distils it with concentrated chromic acid (which does not alter the cumene), distils (whereby the bad smell is completely destroyed, and the pleasant odour of cumene becomes perceptible), and dries over chloride of calcium.

2. *From the Resin of Pinus maritima.*—When the brown oil obtained in the preparation of illuminating gas by the dry distillation of this resin, is subjected to fractional distillation, benzylene passes over between 130° and 160° C., and then cumene. The latter is several times distilled, with separation of the first portion of the distillate, which contains toluene, then treated alternately with oil of vitriol and caustic potash, and each time distilled, and finally rectified two or three times over potassium. (Pelletier and Walter.)

3. *From Light Coal-tar Naphtha*, passing over between 140° and 145° C. (Mansfield); between 139° and 140°. (Ritthausen).—It exists in the naphtha in considerable quantity, and may be advantageously prepared therefrom.

4. *From crude Wood-spirit.*—When the oil separated from this liquid by water is shaken up with oil of vitriol, washed with potash-ley and water, dried over chloride of calcium, and distilled over phosphoric anhydride, and the portion which distils between 140° and 150° C. is subjected to fractional distillation, cumene passes over between 145° and 148°. (Cahours.)

**Properties.**—Cumene is a colourless strongly refracting oil, having an agreeable odour like that of benzene, and a pungent, somewhat bitter taste. Specific gravity 0·87 (Pelletier and Walter). Boils at 144° C. (Gerhardt and Cahours); at 148° (Abel and Cahours). Vapour density = 4·0 to 4·3 (obs.); 4·16 (calc. 2 vols.). Its composition is shown in the following table:

	Calculation.		Pelletier and Walter.	Gerhardt and Cahours.	Abel.	Liës.
C <sup>o</sup>	108	90	89·48	89·81	90·34	88·57
H <sup>12</sup>	12	10	10·08	9·97	9·88	10·28
C <sup>8</sup> H <sup>12</sup>	120	100	99·56	99·78	100·22	98·85



Cumene is insoluble in water, but dissolves readily in *wood-spirit, alcohol, ether, and volatile oils*. It combines with *fixed oils, fats, and most resins*. With the aid of heat it dissolves *sulphur*, which crystallises out on cooling; it also dissolves *iodine*.

**Decompositions.**—1. Cumene is converted by fuming *sulphuric acid* into sulphocumenic acid (Gerhardt and Cahours).—2. When *chlorine* is passed into boiling cumene, and the volatilised portion is cohobated, a thick faint-smelling oil is obtained, which burns slowly with a smoky green-edged flame; its vapour does not attack the eyes (Pelletier and Walter).—3. By fuming *nitric acid*, it is converted into nitrocumene (Cahours, Nicholson), also by boiling with strong nitric acid, but by continued boiling it forms a peculiar acid (Gerhardt and Cahours). If the boiling be continued, the nitrocumene disappears again, and is gradually converted into a yellowish crystalline mass, which dissolves in ammonia, with the exception of a small pulverulent residue. Hydrochloric acid added to the solution precipitates nitrobenzoic acid (Abel, Cahours). Dilute nitric acid converts cumene, after four or five days' boiling, into benzoic acid (Abel).—4. A mixture of *fuming nitric and fuming sulphuric acid* slowly converts cumene into dinitrocumene (Cahours).—5. *Potassium* kept for some time in contact with cumene, blackens and becomes covered with a black crust, which appears to be carbide of potassium (Pelletier and Walter). Cumene is not altered by potash-ley or by fused potash.

**Nitrocumene.**  $C^9H^{11}(NO^2)$ . (Cahours, *Compt. rend.* xxv. 552, xxvi. 315. Nicholson, *Chem. Soc. Qu. J. i. 2.* Ritthausen, *J. pr. Chem.* lxi. 79.)—When cumene is dissolved in fuming nitric acid, the mixture becomes hot and gives off abundance of red vapours, and on adding water to the liquid, nitrocumene is precipitated as a heavy oil. It is yellowish, and has a fainter and less agreeable odour than nitrobenzene. By sulphuretted hydrogen in presence of alcohol and ammonia, it is converted into cumenylamine.

**Dinitrocumene.**  $C^9H^{10}(NO^2)^2$ .—Obtained by treating cumene with a mixture of fuming nitric and fuming sulphuric acid. The action takes place with difficulty, and requires frequent renewal of the acid to complete it.

Dinitrocumene crystallises from alcohol in white laminae. It is insoluble in caustic alkaline leys, but dissolves in alcoholic potash and is converted thereby into nitrobenzylene; hydrochloric acid added to the solution throws down brown flakes. (Cahours, Ritthausen, *loc. cit.*)

**CUMENE-SULPHURIC ACID.** See CUMENYL-SULPHUROUS ACID.

**CUMENGITE.** A crystallised mineral from the province of Constantine in Africa, containing, according to Cumenge (*Ann. Min.* [4] xx. 81), 20 at. antimony, 21 at. oxygen, and 16 at. water. Rammelsberg (*Mineralchemie*, p. 156) suggests that it may be a hydrate of antimoniac acid,  $Sb^2O^3 \cdot 4H^2O$  (or  $2H^3SbO^4 \cdot H^2O$ ).

**CUMENYL.**  $C^9H^{11}$ .—A monobasic radicle which may be supposed to exist in cumene, cuminic acid, and many allied compounds. Thus:

Cumene (Hydrate of Cumenyl) . . . . .	=	$C^9H^{11}.H$
Cumidine (Cumenylamine) . . . . .	=	$C^9H^{11}.H^2.N$
Cumonitrile (Cyanide of Cumenyl) . . . . .	=	$C^9H^{11}.CN$
Cumene-sulphuric or Sulphocumenic acid (Cumenyl- sulphurous acid) . . . . .	=	$C^9H^{11}.H \left. \begin{array}{l} \text{ } \\ \text{ } \end{array} \right\} O^2$ $(SO^2)$
Cumic or Cymylic Alcohol . . . . .	=	$CH^2.C^9H^{11} \left. \begin{array}{l} \text{ } \\ \text{ } \end{array} \right\} O$ $H$
Cumyl . . . . .	=	$CO.C^9H^{11}$
Cuminic Aldehyde or Cuminol . . . . .	=	$CO.C^9H^{11} \left. \begin{array}{l} \text{ } \\ \text{ } \end{array} \right\}$ $H$
Cuminic Acid . . . . .	=	$CO.C^9H^{11} \left. \begin{array}{l} \text{ } \\ \text{ } \end{array} \right\} O$ $H$

It will be seen from these formulæ, that cumene, cuminic alcohol, cuminol, and cuminic acid are related to one another in the same manner as marsh-gas, ethylic alcohol, acetic aldehyde, and acetic acid.

The name *cumenyl* has also been applied to  $C^{10}H^{12}$ , the radicle which is to cymylic alcohol as ethyl to common alcohol; but this creates confusion.

**CUMENYLAMINE.** *Cumidine*,  $C^9H^{12}N = N.H^2.C^9H^{11}$ . Cahours [1847], *Compt. rend.* xxiv. 557; xxvi. 315; xxx. 321. Ed. Chambers Nicholson, *Ann. Ch. Pharm.* lxxv. 58; *Chem. Soc. Qu. J. i. 2.* A. W. Hofmann, *Ann. Ch. Pharm.* lxxvi. 145; lxxiv. 15. Ritthausen, *J. pr. Chem.* lxi. 79. Church, *Phil. Mag.* [4] ix. 454.)

**Formation.**—By the action of sulphydric acid on nitrocumene,  $C^9H^{11}(NO^2)$ , in presence of alcohol and ammonia.



**Preparation.**—Nitrocumene is dissolved in alcohol, and the solution is saturated, first with ammonia, then with sulphydric acid. After a few days, when a large quantity of sulphur has been deposited and the odour of sulphydric acid is no longer perceptible, the gas is again passed through the solution and the liquid is distilled, whereby the decomposition of the sulphydric acid is accelerated; and this treatment is repeated till the whole of the nitrocumene has disappeared. The alcohol and sulphide of ammonium are then removed by distillation; the residue is dissolved in hydrochloric acid; the liquid filtered from the sulphur is evaporated till it solidifies in a crystalline mass on cooling; and the boiling solution of hydrochlorate of cumenylamine is treated with potash to separate the base, which rises to the top of the liquid as an oily layer. This oil is rectified and supersaturated with a concentrated solution of oxalic acid; the liquid is evaporated to dryness; the residue dissolved in boiling alcohol; and the solution treated with blood-charcoal; the filtrate, on cooling, deposits perfectly pure colourless prisms of oxalate of cumenylamine. This salt is dissolved in water; the solution decomposed by potash; and the layer of oil which rises to the surface is removed with a pipette, dried over chloride of calcium, and rectified. (Nicholson.)

**Properties.**—Pale yellow, or, when recently distilled, nearly colourless oil, of specific gravity 0.9526. Refracts and disperses light strongly. When cooled by a mixture of ice and salt, it solidifies in a mass of square plates, which quickly melt again as the temperature rises. Dropped upon paper, it forms a grease-spot, which gradually disappears. In contact with platinum-wire, it boils constantly at  $225^{\circ}\text{C}$ ., when the barometer stands at 0.761 met. It has a peculiar odour and burning taste. Neutral to turmeric and red litmus paper. Colours fir-wood intensely yellow (like phenylamine and benzylamine), but does not exhibit the reaction of phenylamine with chloride of lime. It dissolves very sparingly in water; very easily in sulphide of carbon, wood-spirit, alcohol, ether, and fat oils. (Nicholson.)

**Decompositions.**—1. Cumenylamine exposed to the air, even for a few minutes only, turns yellow and then dark red, especially if warmed.—2. The vapour burns with a yellow, very fuliginous flame.—3. It is violently attacked by *chlorate of potassium* and *hydrochloric acid*, and converted into a brown viscid mass, which smells strongly like trichlorophenic acid, and is dissolved by alcohol, leaving a residue of chloranil.—4. By *bromine* it is converted, with rise of temperature and evolution of hydrobromic acid, into a solid mass, which is insoluble in water, but soluble in alcohol and ether, crystallises in white needles, and is perhaps tribromocumenylamine ( $\text{C}^9\text{H}^{10}\text{Br}_3\text{N}$ ).—5. Strong *nitric acid* dissolves cumenylamine with splendid purple colour, and water added to the liquid throws down flakes which appear to be an acid.—6. Dry *chromic acid* becomes very hot in contact with cumenylamine, but does not set it on fire.—7. In phosgene-gas, cumenylamine is immediately converted into a crystalline mass, which separates from alcohol in long crystals like nitre; probably *dicumenylcarbamide*  $\text{N}^2\text{H}^2(\text{C}^9\text{H}^{11})_2(\text{CO})$ , homologous with diphenylcarbamide or carbanilide.—8. Cumenylamine dissolves in *sulphide of carbon*, and then gives off a large quantity of sulphuretted hydrogen; water added to the solution throws down, after a long time, a quickly solidifying oil, which crystallises from alcohol in long needles; probably *dicumenylsulphocarbamide*,  $\text{N}^2\text{H}^2(\text{C}^9\text{H}^{11})_2(\text{CS})$  (Nicholson).—9. When dissolved in water, it is converted by *cyanogen gas* into cyanocumenylamine (Hofmann).—10. With *cyanate of phenyl*, it immediately solidifies to a solid crystalline mass. (Hofmann.)

**Salts of Cumenylamine.** Cumenylamine is a very weak base. It precipitates sesquioxide of iron from ferric salts. It does not precipitate alumina or zinc-salts. Its salts crystallise very easily, and, with the exception of a few double salts containing chlorides of the heavy metals, they are colourless, but turn reddish on exposure to the air, or when dried at a very high temperature. They have an acid reaction and are anhydrous, like the salts of phenylamine. From concentrated solutions of cumenylamine-salts, alkalis separate the cumenylamine in dark oil-drops, and from dilute solutions in the form of a curd. All the salts of cumenylamine dissolve in water, but better in alcohol. (Nicholson.)

*Acetate of Cumenylamine* crystallises readily.

*Hydrobromate of Cumenylamine* crystallises readily.

*Hydrochlorate of Cumenylamine*,  $\text{C}^9\text{H}^{11}\text{N.HCl}$ .—The combination of cumenylamine with hydrochloric acid is attended with evolution of heat. The salt crystallises from water or alcohol in large, colourless, inodorous prisms, which turn red in the air when moist. It does not undergo any alteration at  $100^{\circ}\text{C}$ ., but melts and sublimates when strongly heated.

*Chloroplatinate of Cumenylamine*,  $\text{C}^9\text{H}^{11}\text{N.HCl.PtCl}_2$ .—When a warm aqueous solution of hydrochlorate of cumenylamine is mixed with excess of dichloride of platinum,

the liquid, on cooling, deposits long yellow needles, which may be obtained pure by washing with cold water. The salt is decomposed by boiling water. When heated *per se* to 100° C., it becomes darker, without further alteration, and at a stronger heat, gives off hydrochlorate of cumenylamine, and leaves platinum. Alcohol dissolves it in large quantity; and the solution yields, after a while, dark red oil-drops, which solidify, after the alcohol has evaporated, in a crystalline mass of a splendid orange-yellow colour.

With *Protochloride of Palladium*, hydrochlorate of cumenylamine forms a double salt, resembling the chloroplatinate in appearance.

*Sulphate of Copper* forms, with alcoholic cumenylamine, a precipitate of a fine green colour.

*Protochloride* and *Cyanide of Mercury* form, with alcoholic cumenylamine, white crystalline precipitates which are decomposed by boiling water.

With *Trichloride of Gold*, alcoholic cumenylamine forms a violet precipitate, which dissolves with violet colour in a larger quantity of alcohol.

*Hydrofluat* of *Cumenylamine* crystallises.

*Hydriodate of Cumenylamine* crystallises readily: it appears to be the most soluble of the cumenylamine salts.

*Nitrate of Cumenylamine*,  $C^9H^{11}N.HNO^3$ .—When cumenylamine is dissolved in dilute nitric acid, the liquid becomes filled, on cooling, with long needles, which are colourless if the acid used was not too strong. The salt remains unaltered at 100° C. It is soluble in water and in alcohol.

With *oxalic acid*, cumenylamine forms a neutral and an acid salt, which are both crystallisable, but cannot be separated. By dry distillation, they yield a slightly crystalline mass, which dissolves sparingly in alcohol, and exhibits the relations of oxycumenylamine. (Nicholson.)

*Phosphate of Cumenylamine* crystallises readily.

*Sulphate of Cumenylamine*,  $2C^9H^{11}N.H^2SO^4$ .—When cumenylamine is dissolved in boiling dilute sulphuric acid, the solution, solidifies, on cooling, in a crystalline mass, which may be obtained perfectly pure by recrystallising with animal charcoal. Inodorous; has an unpleasantly bitter taste. At 100° C. it gives off the odour of cumenylamine, and assumes a reddish colour, without further alteration. Dissolves sparingly in cold water, much more readily in alcohol.

*Cyanocumenylamine*,  $C^9H^{11}N.CN$ , or  $2C^9H^{11}N.Cy^2$ .—An alcoholic solution of cumenylamine saturated with cyanogen quickly deposits long needles of cyanocumenylamine, which are easily purified by crystallisation from alcohol. This substance forms, with hydrochloric acid, a salt nearly insoluble in water. (Hofmann, Ann. Ch. Pharm. lxi. 146.)

*Nitrocumenylamine*,  $C^9H^{12}(NO^2)N$ . (Cahours, Compt. rend. xxiv. 557; xxvi. 315.)—Prepared by treating an alcoholic solution of dinitrocumene with sulphide of ammonium. It forms yellow crystalline scales, which melt below 100° C., and solidify in a radiating mass on cooling. The compound exerts a slight but distinct alkaline reaction on test-paper. It is insoluble in water, but dissolves readily in alcohol and ether.

It is partially decomposed by distillation; nevertheless the greater part passes over unaltered.—*Bromine* acts violently upon it, converting it into a crystalline product, which is no longer basic.—It is not altered by *chloride of benzoyl* at ordinary temperatures; but between 50° and 60° C. it is converted, with violent action, into a crystalline product, which, when dissolved in alcohol, after being washed with acid, alkaline, and pure water, crystallises in snow-white needles, containing  $C^9H^9N^2O^2 = N.(C^9H^9O.NO^2.C^9H^{11})$ , *nitride of benzoyl, cumenyl and nitryl*, corresponding therefore to benzamide and benzanilide.—With *chloride of cumyl* and *chloride of cinnamyl*, it forms products similar to that with chloride of benzoyl.

Nitrocumenylamine neutralises acids completely, even the strongest, forming salts which crystallise well. These salts, if exposed to air in the moist state or in solution, decompose quickly, assuming a greenish-blue colour.

The *sulphate*,  $2C^9H^{12}(NO^2)N.H^2SO^4 + aq.$ , is obtained by dissolving nitrocumenylamine in hot dilute sulphuric acid, and leaving the solution to cool slowly. Long needles having a strong lustre. May be pulverised.

*Hydrochlorate*.—The saturated solution yields, by slow cooling, white silky needles, which, in the dry state, are composed of  $C^9H^{12}(NO^2)N.HCl + aq.$

The *oxalate* forms slender needles.

**CUMENYL-SULPHUROUS ACID.** *Cumene-sulphuric, Sulphocumenic, Sulphocumolic, or Sulphocumenylic acid.*  $C^9H^{12}SO^2 = \frac{(SO)^2}{C^9H^{11}.H} O^2$ . (Gerhardt and

Cahours, Ann. Ch. Phys. [3] i. 90.)—This acid is produced by the action of fuming sulphuric acid on cumene. It is not known in the free state, but the barium-salt may be prepared as follows:—2 pts. of fuming oil of vitriol are poured upon 1 pt. of cumene in a glass cylinder, and the liquid is stirred till the whole of the cumene is dissolved. When large quantities are used, the whole may be left to stand in a closed vessel, the cumene then dissolving gradually. The dark-brown solution is diluted with 4 volumes of water, whereupon, if the cumene and the acid have been long enough in contact, a colourless solution is formed, without separation of cumene; and the liquid, saturated with pulverised carbonate of barium, then filtered and evaporated, yields, on cooling, cumenylsulphite of barium. The colourless mother-liquor yields, to the last drop, the same salt, which may be obtained pure by pressure between paper.

*Cumenyl-sulphite of Barium*,  $C^6H^{11}BaSO_3$ , forms very beautiful scales, having a strong pearly lustre. It dissolves very easily in water, especially when hot. It is soluble in alcohol, even in anhydrous alcohol, and likewise in ether.

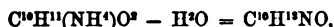
The aqueous solution does not precipitate chloride of cadmium, neutral acetate of lead, or the salts of bismuth, nickel, copper, or mercury.

**CUMIOL.** A name sometimes applied to the radicle of cymylic alcohol,  $C^6H^{10}.H.O$ .

**CUMIN, OIL OF.** A volatile oil obtained from the seeds of *Cuminum Cuminum* by extraction with absolute alcohol and precipitation by water. It is a mixture of cuminol (p. 182) and cymene.

**CUMINAMIC ACID.** See OXYCUMINAMIC ACID (p. 179).

**CUMINAMIDE or CUMYLAMIDE.**  $C^6H^{11}NO = N.H^2.C^6H^{10}$ . (Field, Ann. Ch. Pharm. lxx. 46.)—This compound is obtained by the action of heat on cuminate of ammonium:



or by the action of ammonia on cuminate of ethyl, chloride of cumyl, or cuminic anhydride. Like benzamide, it crystallises in two different forms, according to the manner in which it is deposited. By rapid crystallisation from a strong solution, it is obtained in highly lustrous tables, whereas a dilute solution deposits it in long opaque needles. It dissolves sparingly in cold water, easily in alcohol and in ether. It offers considerable resistance to the action of strong alkalis, and requires long boiling with an acid or an alkali to convert it into ammonia and cuminic acid.

*Cumophenamide* or *Cumanilide*,  $C^6H^{11}NO = N.C^6H^{10}.O.C^6H^5.H$ , is produced by the action of chloride of cumyl on phenylamine. The mixture becomes very hot, and cumophenamide is formed, which, when purified by washing with water and crystallisation from alcohol, in which it dissolves but sparingly, forms long satiny needles, resembling benzoic acid. (Cahours, Ann. Ch. Phys. [3] xxiii. 349.)

*Cumo-sulphophenamide*,  $C^6H^{11}NSO^2 = N.C^6H^{10}.O.C^6H^5.SO^2.H$ . (Gerhardt and Chiozza, Ann. Ch. Phys. [3] xvi. 151.)—Sulphophenamide treated with chloride of cumyl in the oil-bath at a moderate heat is rapidly attacked, and on cooling solidifies to an amorphous glassy mass, which may be crystallised from alcohol. If the temperature were allowed to rise too high, cumonitrile and sulphophenic acid would be produced.

The compound forms rectangular prisms with shining, well-developed terminal faces. It is insoluble in boiling water, but dissolves easily in cold and still more in hot alcohol, easily also in aqueous ammonia. It melts at  $161^\circ C$ . When quickly heated in a test-tube, it gives off cumonitrile.

*Cumo-sulphophenargentamide*,  $N.C^6H^{10}.O.C^6H^5.SO^2.Ag$ , is obtained by adding nitrate of silver to a solution of cumo-sulphophenamide in boiling water containing a few drops of ammonia. It forms very light slender needles nearly insoluble in boiling water, easily soluble in ammonia. Decomposes quietly when heated, giving off cumonitrile. (Gerhardt and Chiozza, *loc. cit.*)

*Cumo-sulphophen-argento-diamide*,  $N^2.H^2.Ag.C^6H^5.SO^2.C^6H^{10}$ , is obtained by dissolving the preceding compound in ammonia, and leaving the solution to evaporate. Crystallises in nacreous needles, grouped like a fan. Soluble in alcohol, very slightly soluble in water. When boiled for some time with water, it gives off a little ammonia.

*Cumo-benzo-sulphophenamide*,  $C^6H^{11}NSO^2 = N.C^6H^{10}.O.C^6H^5.O.C^6H^5.SO^2$ . Formed by the action of chloride of cumyl on benzosulphophenargentamide (i. 540), and obtained in confused prisms by dissolving the product in boiling ether and evaporating. It is nearly insoluble in water, more soluble in alcohol, sparingly in ether. Ammonia dissolves it with difficulty, the solution being precipitated by acids and by the salts of lead and silver. (Gerhardt and Chiozza, *loc. cit.*)

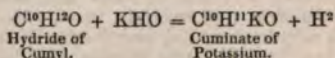


*Cumo-salicylamide*,  $C^{17}H^{17}NO^3 = N.C^{10}H^{11}O.C^7H^5O^2.H?$ —Obtained by the action of chloride of cumyl on salicylamide. Crystallises in very light shining needles, melting at  $200^{\circ} C.$ , becoming pasty at a stronger heat, and remaining so on cooling.

**CUMINIC ACID.**  $C^{10}H^{12}O^2 = C^{10}H^{11}O.H.O.$ , or  $C^{10}H^{12}O^4$ . (Gerhardt and Cahours [1840], Ann. Ch. Phys. [3] i. 70. Gm. xiv. 148.)—This acid is produced by the oxidation of the oxygenated oil (hydride of cumyl) contained in essence of cumin.

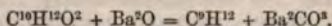
*Preparation.*—Hydride of cumyl is added drop by drop to potash in the state of fusion, whereupon hydrogen is evolved and cuminate of potassium is formed; and this salt, dissolved in water and decomposed by nitric acid, deposits cuminic acid, which may be purified by crystallisation from alcohol.

The formation of cuminate of potassium in this process is represented by the equation:

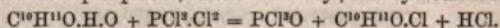


*Properties.*—Colourless prismatic tables, having a pure acid taste and an odour somewhat like that of bugs. It melts at  $92^{\circ} C.$ , and volatilises at about  $250^{\circ}$ . It is nearly insoluble in cold water, but soluble in alcohol and ether. When pure, it dissolves without colour in strong sulphuric acid.

*Decompositions.*—1. *Fuming nitric acid* converts cuminic acid into nitrocuminic acid; with a mixture of *nitric* and *sulphuric* acids, it yields dinitrocuminic acid. 2. By dry distillation with *baryta* or *lime*, it is resolved into cumene,  $C^9H^{12}$ , and carbonic acid:



3. With *pentachloride of phosphorus*, at a temperature not exceeding  $50^{\circ}$  or  $60^{\circ} C.$ , it yields oxychloride of phosphorus, chloride of cumyl, and hydrochloric acid:



4. *Oxychloride of phosphorus* converts cuminate of sodium into cumini canhydride (Gerhardt).—5. Cuminic acid boiled with *acid chromate of potassium* and *sulphuric* acid is converted into insolinic acid,  $C^9H^8O^4$  (Hofmann, Ann. Ch. Pharm. xlvii. 197).—6. Cuminic acid heated with *bromide of cyanogen* yields cumonitrile and bromide of potassium.—7. The sodium-salt heated with *chloride of cumyl*, *acetyl*, or *benzoyl*, yields cuminic, acetocuminic, or benzocuminic anhydride (Gerhardt).—8. Cuminic acid does not undergo any transformation in passing through the animal organism, but is found in the urine unaltered.

**CUMINATES.**—Cuminic acid is monobasic, the formula of its salts being  $C^{10}H^{11}MO^2$ .

*Cuminate of ammonium* forms delicate tufts which lose their lustre when exposed to the air. When heated, it gives up the elements of water and yields cuminamide and cumonitrile. The *potassium-salt* is deliquescent, and cannot be obtained in regular form.

*Cuminate of barium*,  $C^{10}H^{11}BaO^2$ , is obtained in dazzling white nacreous scales by decomposing carbonate of barium with a solution of cuminic acid. With a hot concentrated solution, the salt is precipitated immediately on passing through the filter; and each crystal, at the moment of its formation, reflects the light with great vividness, exhibiting all the tints of the spectrum.—*Cuminate of calcium* forms small needles moderately soluble in water.—*Cuminate of copper* is light blue and insoluble in water.—*Cuminate of lead*. White precipitate, insoluble in water.

*Cuminate of silver*,  $C^{10}H^{11}AgO^2$ , is obtained by adding nitrate of silver to cuminate of ammonium. It is white, curdy, and blackens rapidly when exposed to the light. When calcined, it leaves a residue of carburet of silver,  $CAg^4$ , of a dull yellow colour. By dry distillation, it yields carbonic anhydride, cuminic acid, and cumene.

#### Derivatives of Cuminic Acid.

**Nitrocuminic Acid.**  $C^{10}H^{11}(NO^2)O^2$ . (Gerhardt and Cahours, Ann. Ch. Phys. [3] i. 73; Cahours, *ibid.* xxv. 36.)—Produced by the action of fuming nitric acid on cuminic acid. On boiling the mixture, and then adding water, the nitrocuminic acid separates as a heavy yellow oil, which soon solidifies. It is triturated, washed with distilled water, and crystallised from alcohol.

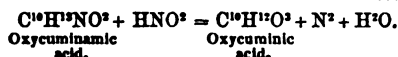
Nitrocuminic acid forms yellowish-white scales, insoluble in water, easily soluble in alcohol and ether. It dissolves in ammonia, potash, and soda, forming crystallisable salts. The *calcium-salt*,  $C^{10}H^{10}Ca(NO^2)O$ , crystallises in stellate groups of yellow needles, which become darker when exposed to light. The *silver-salt*,  $C^{10}H^{10}(NO^2)AgO^2$ , is a white precipitate insoluble in water.

**Dinitrocuminic Acid.**  $C^{10}H^{10}(NO^2)^2O^2$ . (Cahours, Ann. Ch. Phys. [3] xxv. 37.)—When cuminic acid is added by small portions to a gently heated mixture of fuming nitric and sulphuric acid, it disappears without evolution of gas. On boiling the liquid,

red vapours are evolved, and nitrocuminic acid is deposited in shining yellow scales, which may be recrystallised from boiling alcohol. It dissolves also readily in ether. It is not acted upon by fuming nitric acid, even after long boiling. It does not dissolve in caustic ammonia, potash, or soda, or appear to combine with them by long boiling. *Hydrogen* in the nascent state (from acetic acid and iron) converts it into dioxycuminamic acid (p. 180).

According to Cahours, dinitrocuminic acid does not combine with bases, and is insoluble in aqueous potash, soda, or ammonia, even at the boiling heat; according to Kraut, on the other hand (Chem. Centr. 1869, p. 85), it unites with bases, forming yellowish-red salts which become darker on exposure to light. The *barium-salt*  $C^{10}H^7Ba(NO_2)_2O^2$ , is obtained by dissolving the acid in baryta water, precipitating the excess of baryta with carbonic acid, then boiling, filtering, and evaporating: it separates in films which become crystalline on standing. The *calcium-salt*,  $C^{10}H^7Ca(NO_2)_2O^2$ , prepared in like manner, forms yellow-red needles, which dissolve easily and with deep wine-red colour in boiling water. The *silver-salt*,  $C^{10}H^7Ag(NO_2)_2O^2 + aq.$ , obtained by precipitating the calcium-salt with nitrate of silver, and recrystallising the precipitate from boiling water, forms light yellow needles, which are scarcely altered by light, but when heated to  $100^\circ C.$  give off 5 per cent. (= 1 at.) water. (Kraut.)

**Oxycuminic Acid.**  $C^{10}H^{12}O^2$ . (Cahours, Ann. Ch. Phys. [3] liii. 338.)—This acid, regarded by Kolbe as  $C^{10}H^{11}(HO)O^2$ , that is, as derived from cuminic acid by the substitution of HO for 1 at. hydrogen, is produced by the action of nitric oxide or nitrous acid on oxycuminamic acid dissolved in a moderate excess of nitric acid:



It separates in small brownish prisms, sparingly soluble in cold water, more soluble in boiling water, still more in alcohol. It unites with bases, and some of its salts crystallise well. The silver-salt has the composition  $C^{10}H^{11}AgO^2$ .

**Oxycuminamic acid**,  $C^{10}H^{11}NO^2 = N.H^2.(C^{10}H^{10}O^2)^{\cdot}H.O$ , or *Amidocuminic acid*,  $C^{10}H^{11}(NH^2)O^2$ , also called *Cuminamic acid*.—This acid, the homologue of oxybenzamic acid, was discovered by Cahours (Ann. Ch. Phys. [3] liii. 822.) It is produced by the reduction of nitrocuminic acid, either with sulphydric acid, or with ferrous acetate.

**Preparation.**—1. Nitrocuminic acid is reduced by excess of sulphydric acid; the liquid is evaporated at a gentle heat till all the ammonia is expelled and the excess of sulphur is separated; the concentrated solution is precipitated by a slight excess of acetic acid; and the resulting precipitate is collected, washed, dried, and recrystallised from alcohol (Cahours).—2. It is also obtained by treating nitrocuminic acid with iron filings and acetic acid (a brisk action then taking place, attended with rise of temperature, after which the mixture must be heated for a while in the water-bath), digesting the mixture with aqueous carbonate of sodium, filtering, neutralising the excess of soda with acetic acid, precipitating with acetate of lead, and decomposing the precipitate with sulphydric acid. (Bouillet, Compt. rend. xliii. 399.)

The acid forms colourless or light-yellow crystals, sparingly soluble in cold, more soluble in hot water; also in alcohol and in ether.

**Decompositions.**—1. In solution in nitric acid, it is converted by nitric oxide gas into oxycuminic acid.—2. By treating alcoholic oxycuminamic acid with nitrous acid, light yellow needles are obtained, consisting of a new dibasic acid =  $C^{10}N^2H^{10}O^4$  (P. Griess, Compt. rend. xlix. 80):



This acid, regarded by Griess as diazocumin-amidocuminic acid, =  $C^{10}H^{10}N^2O^4$ ,  $C^{10}H^{11}(NH^2)O^2$ , forms yellow crystals, insoluble in water, and nearly insoluble in alcohol and ether.—3. Oxycuminamic acid distilled with caustic baryta or lumps of potash, yields an alkaline carbonate together with cumenylamine.

**Combinations.**—Oxycuminamic acid unites with bases, but its metallic salts have not been examined. The ethyl-compound,  $C^{10}H^{11}(C^2H^3)NO^2$ , is obtained by reducing nitrocuminic acid of ethyl with sulphide of ammonium, or with iron filings and acetic acid. It is a heavy oil, which dissolves in hydrochloric, nitric, and sulphuric acid, forming crystallisable compounds. Ammonia decomposes it slowly, forming a substance probably analogous to phenyl-urea.

Oxycuminamic acid likewise unites with other acids, forming crystalline salts.

**Hydrochlorate**,  $C^{10}H^{11}NO^2.HCl$ .—Oxycuminamic acid dissolves slightly in boiling hydrochloric acid, and the solution on cooling deposits thin needles. The compound may also be prepared by adding alcohol to a mixture of oxycuminamic acid and hydrochloric acid, whereby a considerable quantity of oxycuminamic acid is dissolved,



and evaporating. Delicate shining prisms, which dissolve in water, and are partly precipitated on addition of hydrochloric acid.

The *chloroplatinate*,  $C^{10}H^{12}NO^2.HClPtCl^2$ , is obtained by adding alcohol to the mixed solutions of concentrated dichloride of platinum and hydrochlorate of oxycuminamic acid, warming the mixture till it dissolves, then filtering and leaving the solution to evaporate. It forms long reddish needles.

The *nitrate* forms beautiful prisms.

*Sulphate*,  $2C^{10}H^{12}NO^2.H^2SO^4$ .—Oxycuminamic acid is mixed in slight excess with oil of vitriol diluted with an equal bulk of water, and the mixture is dissolved in warm alcohol. On cooling, thin, white, silky needles are deposited. The compound has a slightly sweet taste, dissolves sparingly in cold, easily in hot water.

**Dioxycuminamic acid**,  $C^{10}H^{10}N^2O^2 = N^2.H^4.(C^{10}H^8O)^{''}$ .H.O., or *Diamidocuminic acid*,  $C^{10}H^{10}(NH^2)^2O^2$ : also called *Dicuminamic acid*.—This acid, the homologue of dioxybenzamic acid, is obtained by reducing dinitrocuminic acid with iron filings and acetic acid, the mode of preparation being similar to that of oxycuminamic acid. It is crystallisable, and unites with bases (Boulet, *Compt. rend.* xliii. 399). The first of the above rational formulae represents the compound as a diamic acid derived from a hypothetical dioxybenzoic acid,  $C^{10}H^{12}O^4$ , containing the triatomic radicle  $C^{10}H^8O$ .

**CUMINIC ALCOHOL**. Syn. with CUMYLIC ALCOHOL (*q. v.*)

**CUMINIC ALDEHYDE**. Syn. with HYDRIDE OF CUMYL (*p.* 182).

**CUMINIC ANHYDRIDE**. *Anhydrous Cuminic acid*. *Cuminate of Cumyl*,  $C^{10}H^{22}O^2 = (C^{10}H^{11}O)^2O$ .—[Gerhardt (1852), *Ann. Ch. Phys.* [3] xxxvii. 304].—Produced by the action of chloride of cumyl on cuminate of sodium. The two substances, perfectly dry, are heated together in a flask, till the odour of chloride of cumyl completely disappears. A syrupy mass is then left, which, when treated with hot water, yields the anhydride. The product may be purified by recrystallising it several times from pure ether.

Cuminic anhydride, recently prepared, is oily, tasteless, nearly colourless, and inodorous, but soon experiences a molecular change, by which it is converted into a mass of very brilliant rhomboïdal crystals. In moist air, it is rapidly converted into cuminic acid. With ammonia it forms cuminamide.

**CUMINACETIC ANHYDRIDE**. See ACETO-CUMINIC ANHYDRIDE. (*i.* 21.)

**CUMINO-BENZOIC ANHYDRIDE**. See BENZO-CUMINIC ANHYDRIDE. (*i.* 558.)

**CUMINO-EUGENIC ANHYDRIDE**. *Cuminate of Eugenyl*,  $C^{20}H^{22}O^2 = C^{10}H^{11}O.C^{10}H^{11}O.O$ .—Isomeric with cuminic anhydride; obtained by heating eugenic acid with chloride of cumyl. Crystallises in colourless, very brilliant plates, which melt very easily, but do not volatilise below  $400^{\circ}C$ . It is not decomposed by boiling potash-ley, but when fused with hydrate of potassium, it is resolved into cuminate and eugenate of potassium. Sulphuric acid decomposes it in a similar manner. Fuming nitric acid decomposes it readily, producing a reddish-yellow tenacious mass, in which crystals may be observed. Hydrochloric acid does not act upon it, even at boiling heat. (Cahours, *Ann. Ch. Phys.* [3] xli. 491.)

**CUMIN-ENANTHYLIC ANHYDRIDE**. *Cuminate of Enanthyl*,  $C^{17}H^{24}O^2 = C^{10}H^{11}O.C^7H^{13}O.O$ .—Produced by the action of chloride of cumyl on enanthylate of potassium. It is an oily liquid, heavier than water, and smelling like apples. Its vapour excites coughing. (Chiozza and Malerba, *Gerh. Traité*, iii. 601).

**CUMO-SALICYLOUS ANHYDRIDE**. *Cuminate of Salicyl*, *Cumosalicyl*,  $C^{17}H^{16}O^4 = C^{10}H^{11}O.C^7H^5O^2.O$ . (Cahours, *Ann. Ch. Phys.* [3] lii. 107).—Obtained by heating salicylous acid with chloride of cumyl. Crystallises in colourless, shining, friable prisms, which melt to a clear oil at a gentle heat, and solidify on cooling. Insoluble in cold water, slightly soluble in boiling water; soluble in alcohol, especially when warm; insoluble in ether. With *chlorine*, *bromine*, and *fuming nitric acid*, it yields crystallisable products. It is not attacked by solid caustic potash or by aqueous potash, even at the boiling heat.

**CUMO-METHYL-SALICYLIC ANHYDRIDE**. *Cuminate of Methyl-salicyl*,  $C^{15}H^{18}O^4 = C^{10}H^{11}O.C^5H^7(CH^3)O^2.O$ . (Gerhardt, *Traité*, iii. 317).—Produced by heating chloride of cumyl with salicylate of methyl (oil of wintergreen). The product is a viscid oil which remains fluid for a long time, but if a small quantity of ether is poured into it, it solidifies in a radiated mass as the ether evaporates. It crystallises from boiling alcohol in very brilliant rhombic scales, insoluble in cold water, sparingly soluble in cold alcohol, very soluble in ether, which, as it evaporates, deposits the compound in rhomboïdal prisms, often of considerable size. From a hot saturated alcoholic solution, it is deposited as an oil which remains liquid for a considerable time.



**CUMINIC ETHERS.** *Cuminate of Ethyl.*  $C^{10}H^{14}O^2 = C^{10}H^{11}O^2.C^2H^3$ .—Obtained by passing hydrochloric acid gas into a solution of cuminic acid in absolute alcohol, till it is no longer absorbed, then heating the liquid over the water-bath to expel the excess of alcohol, distilling the residue over the naked fire, washing the distillate with carbonate of sodium, and rectifying over massicot. It is a colourless liquid, lighter than water, and having an agreeable odour of apples. It boils at  $240^{\circ}C$ ., giving off a vapour which easily takes fire and burns with a bluish flame. Index of refraction of the liquid, 1.504. Vapour-density, 6.65. When heated with solution of potash, it yields alcohol and cuminate of potassium.

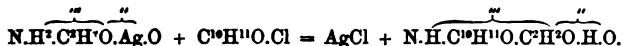
*Cuminate of Phenyl.*  $C^{10}H^{14}O^2 = C^{10}H^{11}O.C^6H^5.O$ . (Williamson and Scrugham, Proc. Roy. Soc. vii. 18.—Kraut, *Dissertation über Cuminal und Cymen*, 1854.)—Produced: 1. By the action of chloride of cumyl on phenate of potassium (W. and Scr.).—2. By the dry distillation of cumo-salicylic acid, or of a mixture of equivalent quantities of chloride of cumyl and salicylate of sodium (Kraut). Crystallises in long white needles, melting between  $57^{\circ}$  and  $58^{\circ}C$ . and distilling without decomposition. It has an agreeable odour, resembling that of benzoate of phenyl, especially when heated. Insoluble in water, easily soluble in alcohol and ether.

A mixture of this ether with nitrate of sodium, heated with strong sulphuric acid, yields dinitrocuminic (and probably also nitrocuminic) acid. By sulphuric acid alone, it is resolved into cuminic and sulphophenylic acids. It is decomposed by alcoholic (not by aqueous) potash, yielding cuminate and phenate of potassium. (Kraut.)

**CUMINOL.** Syn. of HYDRIDE OF CUMYL (p. 183).

**CUMINURIC ACID.** *Glycol-cuminic acid, Cumyl-oxyacetamic acid,*  $C^{12}H^{14}NO^3$

$= N.H.C^{10}H^{11}O.(C^2H^3O).H.O$ .—This acid, homologous with hippuric (benzoyl-oxyacetamic) acid, is produced by the action of the silver-compound of glycol (oxyacetamate of silver) on chloride of cumyl:



The cuminuric acid is extracted from the product by warm alcohol, and remains on evaporation as a brown mass, which may be purified by pressure and recrystallisation. Its silver-salt is  $C^{12}H^{14}AgNO^3$ . The acid heated with aqueous hydrochloric acid is resolved into glycol and cuminic acid. (Cahours, Ann. Ch. Phys. [3] liii. 356.)

**CUMINYL.**  $C^{10}H^{11}$ . A monatomic radicle, of which cuminol,  $C^{10}H^{12}O$ , may be regarded as the hydrate  $= C^{10}H^{11}.H.O$ .

**CUMMINGTONITE.** See HORNBLÉNDE.

**CUMO-GLYCOL.** Syn. with HYDRATE OF CUMYLENE (hyp.)  $= C^{10}H^{12}.H^2.O^2$ . (See page 184.)

**CUMOL.** Syn. of CUMENE (p. 173).

**CUMONITRILE.**  $C^{10}NH^{11}$ , or *Cyanide of Cumetyl*,  $C^9H^{11}.CN$ . (Fr. Field, Ann. Ch. Pharm. lxx. 61; Mem. Chem. Soc. iii. 408.)

*Formation.*—1. By the dry distillation of cuminate of ammonium, cuminamide being formed at the same time.—2. By the action of bromide of cyanogen on cuminate of potassium, carbonic anhydride being likewise evolved (Cahours, Ann. Ch. Phys. [3] lii. 201):



—3. By the action of heat on cumosulphophenamide and on cumosulphophenargentamide. (Gerhardt and Chiozza, Ann. Ch. Phys. [3] xlii. 167.)

*Preparation.*—Cuminate of ammonium is heated in a retort to complete fusion, and then maintained in violent ebullition, whereupon large drops of cumonitrile pass over together with water. As soon as the oil has completely passed over, it is separated with a pipette from the distillate, and the watery liquid is poured back into the cooled retort, and redistilled five or six times. The whole of the oil thus obtained is freed by washing with ammonia from traces of dissolved cuminic acid; it is then washed successively with hydrochloric acid and water, dried by leaving it for some days over chloride of calcium, and rectified. The portion which goes over last may contain water.

*Properties.*—Transparent, colourless oil, of specific gravity 0.765 at  $14^{\circ}C$ . Refracts light strongly. Boils constantly from platinum wire at  $239^{\circ}C$ ., under pressure of 0.7585 met. Has a very strong but agreeable odour, and a burning taste. It dissolves but slightly in water, and renders it milky. Alcohol and ether dissolve it in all proportions.

*Decompositions.*—1. The vapour of cumonitrile is inflammable, and burns with a brilliant flame.—2. Cumonitrile is but slightly altered by strong *nitric acid* in the cold, but on boiling, cuminic or nitrocuminic acid is produced.—3. Heated with *potassium*, it becomes darker and forms a larger quantity of cyanide of potassium.—4. *Alcoholic potash* does not alter it immediately, but converts it, after a few days, into a crystalline pulp, consisting of the oil turned yellow and cuminamide.

**CUMOPHENAMIDE.** See CUMINAMIDE (p. 177).

**CUMOSALICYL.** Syn. with CUMOSALICYLOUS ANHYDRIDE (p. 180).

**CUMOBENZOSULPHOPHENAMIDE.**

**CUMOSALICYLAMIDE.**

**CUMOSULPHOPHENAMIDE.**

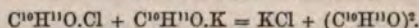
} See CUMINAMIDE (p. 177).

**CUMOXYL.** Syn. with CUMYL.

**CUMOYL.** Weltzien's name for the radicle  $C^{10}H^{11}$ , of which cuminol (*vid. inf.*) may be regarded as the hydrate.

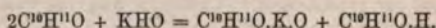
**CUMYL.** *Cumoxyl*,  $C^{10}H^{11}O$ .—An acid organic radicle homologous with benzoyl, and forming a series of compounds corresponding to the benzoyl-compounds, viz. *hydride of cumyl* or *cuminol*,  $C^{10}H^{11}O.H$ ; *hydrate of cumyl*, or *cuminic acid*,  $C^{10}H^{11}O.H.O$ ; *nitride of cumyl and hydrogen*, or *cuminamide*,  $N.H^2.C^{10}H^{11}O$ , &c.

*Cumyl in the free state*, or *Cumylide of Cumyl*,  $C^{20}H^{22}O^2$ , is obtained by the action of chloride of cumyl on an equivalent quantity of cumylide of potassium:



The mixture is gently heated to facilitate the separation of the chloride of potassium, and the resulting mass is treated with a weak solution of potash to decompose the last traces of chloride of cumyl. It is then digested with ether to dissolve out the cumyl, and the ethereal solution is left to evaporate.

Cumyl is an oily liquid, heavier than water; its odour is scarcely perceptible at ordinary temperatures, but becomes very strong under the influence of heat, and resembles that of the geranium. It boils at  $300^{\circ}C$ , decomposing at the same time, and yielding cuminic acid, several substances less highly oxidised than that acid, and carbonaceous matter. It is combustible, and burns with a smoky flame. Heated with potash, it is converted into cuminic acid and hydride of cumyl:



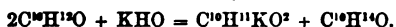
Cumyl dissolves sparingly in cold alcohol, but boiling alcohol dissolves it in considerable quantity. (Chiozza, *Ann. Ch. Phys.* [3] xxxix. 246.)

**CUMYL, HYDRIDE OF.** *Cuminic Aldehyde*. *Cuminol*.  $C^{10}H^{12}O = C^{10}H^{11}O.H$ . (Gerhardt and Cahours, *Ann. Ch. Phys.* [3] i. 60.—Bertagnini *Ann. Ch. Pharm.* lxxxvi. 275.—Kraut, *Dissertation über Cuminol und Cymen*, 1854; *Ann. Ch. Pharm.* xcvi. 366.—Gm. xiv. 148.)—This compound exists in the essential oil of cumin, which is in fact a mixture of cuminol with a hydrocarbon named *Cymene* ( $C^{10}H^{14}$ ). On distilling this essence, the cymene passes over first at about  $200^{\circ}C$ , and afterwards the hydride of cumyl. To obtain this latter in the pure state, it should be distilled as rapidly as possible in an atmosphere of carbonic anhydride. Another mode of separation is to agitate the cumin-oil with a moderately concentrated solution of acid sulphite of potassium or sodium, which takes up the hydride of cumyl, but not the cymene, forming a crystalline compound from which the hydride of cumyl may be separated by potash. Hydride of cumyl also occurs, together with cymene, in the volatile oil obtained from the seeds of the water-hemlock (*Cicuta virosa*), and may be separated by acid sulphite of potassium as above. (Trapp, *Ann. Ch. Pharm.* cviii. 386.)

*Properties.*—Hydride of cumyl is a colourless or slightly yellow liquid, having a strong and persistent odour of cumin, and an acrid burning taste. Boiling point  $220^{\circ}C$ . (Gerhardt and Cahours); from platinum at  $229.4^{\circ}$ , or, correcting for the mercurial column in the thermometer, at  $236.6^{\circ}$  (Kopp). Specific gravity in the liquid state = 0.9727 at  $13.4^{\circ}C$ . = 0.9832 at  $0^{\circ}$  (Kopp.) Vapour-density = 5.24 (obs.) = 5.13 (calc. 2 vols.). Composition, by analysis (mean), 80.89 per cent. carbon, 8.45 hydrogen, and 10.66 oxygen, the formula requiring 81.08 C, 8.11 H, and 10.81 O. It is isomeric with the essential oils of anise, fennel, star-anise, and tarragon.

*Decompositions.*—1. Hydride of cumyl may be distilled without alteration in close vessels, but when boiled for some time in contact with the air, it is converted into cuminic acid, together with a resinous substance. The same transformation takes place even at ordinary temperatures, especially in contact with water, or more quickly in contact with a base.—2. By *fuming nitric acid* in the cold, cuminol is converted into cuminic acid; heated with nitric acid, either strong or weak, it yields nitro-cuminic

acid, together with resinous products.—3. By a mixture of *acid chromate of potassium and sulphuric acid*, it is converted into cuminic acid (Gerhardt and Cahours); by prolonged action into insolinic acid (Hofmann, Ann. Ch. Pharm. xevii. 207).—4. With *chlorine* or *bromine* it forms substitution-products in which 1 at. hydrogen is replaced by chlorine or bromine; but with *pentachloride of phosphorus*, it forms the compound  $C^6H^5Cl^5$ , derived from hydride of cumyl by the substitution of chlorine for oxygen.—5. Dry *ammonia gas* converts cuminol after some time into a substance resembling hydrobenzamide (Gerhardt and Cahours). Sieveking (Ann. Ch. Pharm. cvi. 357) could not obtain this body.—6. *Sulphide of ammonium* decomposes cuminol, forming thiocuminol,  $C^6H^5S$ , in which the oxygen of hydride of cumyl is replaced by sulphur.—7. Heated with *potassium*, it gives off hydrogen and forms cumylide of potassium,  $C^6H^5O.K.$ —8. Cuminol boiled with *aqueous*, or more quickly with *alcoholic potash*, is converted into cuminate of potassium and cymylic alcohol:



—9. Cuminol heated with *solid caustic potash*, yields various products, according to the degree of heat applied and the manner in which the two substances are brought in contact. When the solid potash is covered with cuminol and slightly heated, cumylide of potassium is formed. When cuminol is added by drops to melting potash, the mass first turns red, then quickly white, and forms cuminate of potassium, with elimination of hydrogen:



If, however, the heat applied is comparatively low, cuminic acid and cymene are formed, without evolution of hydrogen:



In this case it may be supposed, that the cuminol is first resolved into cuminic acid and cymylic alcohol, and the latter subsequently into cuminic acid and cymene (Kraut).—10. With chloride of cumyl, cuminol yields hydrochloric acid and cumyl (p. 182).

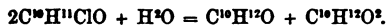
*Combinations.*—Hydride of cumyl unites with the acid sulphites of the alkali-metals, forming crystalline compounds. The *ammonium-salt* crystallises in needles; the *potassium-salt* in scales; the *sodium-salt*,  $C^6H^5O.NaHSO^3$ , in colourless inodorous needles, which become yellow by keeping.

#### Derivatives of Hydride of Cumyl.

**Cumylide of Potassium**,  $C^6H^5O.K.$ —Produced by heating hydride of cumyl with potassium out of contact of air; also by heating solid hydrate of potassium in the midst of hydride of cumyl: in the latter case, water is eliminated and the potash is converted into a gelatinous mass. To obtain pure cumylide of potassium, the product formed by the first process is pressed between filtering paper, and placed in vacuo over sulphuric acid, which absorbs the undecomposed hydride of cumyl.

Cumylide of potassium is an amorphous gelatinous mass, quickly converted into cuminate by contact with the air. Water decomposes it into hydride of cumyl and hydrate of potassium. Heated with chloride of cumyl, it yields chloride of potassium and free cumyl. With chloride of benzoyl, it yields an oil resembling cumyl, probably benzo-cumyl,  $C^6H^5O.C^6H^5O.$  (Gerhardt and Chiozza, *loc. cit.*)

**Chlorocuminol**,  $C^6H^5ClO.$ —Produced by passing dry chlorine through dry hydride of cumyl. It is a yellowish oil, heavier than water and having a very powerful odour. By exposure to moist air, it is converted into hydrochloric and cuminic acids:



It is decomposed by dry distillation, yielding hydrochloric acid and a peculiar oil, and leaving a residue of charcoal. Strong sulphuric acid dissolves it, forming a crimson solution and giving off hydrochloric acid. The liquid exposed to moist air, quickly yields crystals of cuminic acid. Chlorocuminol when recently prepared, is scarcely attacked by ammonia, differing in that respect from the isomeric compound, *chloride of cumyl*, which is immediately transformed by ammonia into cuminamide. (Gerhardt and Chiozza, Ann. Ch. Phys. [3] i. 82.)

**Bromocuminol**,  $C^6H^5BrO.$  is a heavy oil resembling chlorocuminol, and obtained by the action of bromine on hydride of cumyl. (Gerhardt and Chiozza.)

**CUMYL, CHLORIDE OF**,  $C^6H^5O.Cl.$ —Obtained by the action of pentachloride of phosphorus on cuminic acid. It is a colourless very mobile liquid, of specific gravity



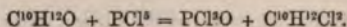
1.070 at 15° C. Boils between 256° and 258° C. By exposure to moist air, or more rapidly by boiling with caustic potash, it is converted into hydrochloric and cuminic acids. It is strongly heated by contact with strong alcohol, yielding hydrochloric acid and cuminate of ethyl.

With dry ammonia gas, or with carbonate of ammonium, it forms cuminamide; with phenylamine it yields phenylcuminamide or cumaniide. (Cahours, Ann. Ch. Phys. [3] xxiii. 347.)

**CUMYLAMIDE.** Syn. with CUMINAMIDE (p. 177).

**CUMYLENE.**  $C^{10}H^{12}$ .—A hypothetical diatomic radicle, homologous with benzylene (i. 577), of which the following compounds are known.

**CHLORIDE OF CUMYLENE.** *Chlorocumol*, *Chlorocuminol*,  $C^{10}H^{12}Cl^2$ . (Cahours, Ann. Ch. Phys. [3] xxiii. 345.—Sieveking, Ann. Ch. Pharm. cvi. 258.—Tüttscheff, J. pr. Chem. lxxv. 370.)—Produced by the action of pentachloride of phosphorus on hydride of cumyl:



It is a limpid oily liquid having, a penetrating but not unpleasant odour, heavier than water and insoluble therein; easily soluble in alcohol and ether. Boils between 255° and 260° C. (Cahours); at 255° with slight decomposition. (Tüttscheff.)

*Decompositions.*—1. Heated with alcoholic ammonia in a sealed tube, it forms chloride of ammonium and a thick yellow oil (Sieveking).—2. It does not appear to be decomposed by aqueous potash (Cahours).—3. With sulphhydrate of potassium it yields chloride of potassium, and a viscid product of repulsive odour (Cahours). By prolonged treatment of the alcoholic solution with sulphide of ammonium, it forms a dark-red resin soluble in ether (Sieveking).—4. Freshly precipitated oxide of silver converts it into cuminol (Tüttscheff).—5. When 2 at. ethylate of sodium are heated with 1 at. chloride of cumylene, chloride of sodium and a red liquid are obtained. When this product is distilled, first alcohol, and then, between 170° and 238° C., an oil passes over, which behaves with acid sulphites of alkali-metals like cuminol (Sieveking).—6. With acetate of silver, it forms acetate of cumylene (Sieveking), with benzoate of silver, benzoate of cumylene. (Tüttscheff.)

**ACETATE OF CUMYLENE.** *Acetate of Cumoglycol*, *Biacetate of Cumol*,  $C^{14}H^{18}O^4 = (C^4H^6O)^2$ . ( $C^{10}H^{12}$ ). $O^2$ . (Sieveking, loc. cit.)—Chloride of cumylene is mixed with excess of acetate of silver, and the reaction, which immediately ensues, is finally aided by a gentle heat. The product is treated with ether; the solution evaporated; and the residue is washed with aqueous carbonate of soda, and crystallised from ether, whereby yellowish crystals, contaminated with an oil, are obtained. When pure it forms colourless crystals, resembling the swallow-tail crystals of gypsum. It melts at a moderate heat, and diffuses a powerful odour of acetic acid and cuminol.

**BENZOATE OF CUMYLENE.** *Benzoate of Cumoglycol*, *Bibenzoate of Cumol*,  $C^{22}H^{26}O^4 = (C^8H^{10}O)^2$ . ( $C^{10}H^{12}$ ). $O^2$ . (Tüttscheff, loc. cit.)—Seven pts. chlorocumol are mixed in a porcelain dish with 16 pts. benzoate of silver; the mass thereby formed is treated with ether, which leaves chloride of silver; and the resulting solution of benzoate of cumoglycol is left to evaporate spontaneously, whereupon a brownish yellow oil, solidifying in crystals in a few days, is deposited. This is pressed between paper, washed with aqueous ammonia, and recrystallised alternately from ether-alcohol and absolute alcohol.

It forms brilliant, colourless needles, melting at 88° C., and solidifying in crystals on cooling; soluble in alcohol, especially in warm strong alcohol, and precipitated by water; soluble in ether, acetone, and chloroform.

It cannot be volatilised without undergoing decomposition. It is dissolved by cold sulphuric acid with dark red colour; the solution blackens by boiling; it is not attacked by boiling nitric acid; it is not affected by ammonia or by concentrated baryta-water; distilled with caustic potash, it yields benzoate of potassium and cuminol.

**CUMYLIC ACID.** Syn. with CUMINIC ACID.

**CUMYL-SALICYLAMIDE.**

**CUMYL-SULPHOPHENAMIDE.**

} See CUMINAMIDE (p. 178).

**CUPEL.** A shallow cup-shaped vessel made of bone-earth rammed into a mould which gives it its shape. It is used in assaying gold and silver with lead. (See GOLD and SILVER.)

**CUPRAMINES, CUPRAMMONIAS, CUPRAMMONIUMS.** Bases derived from the types  $NH^3$  and  $NH^4$  by substitution of one or more atoms of copper for an equivalent quantity of hydrogen (p. 79).

**CUPREOUS ANGLESITE.** See LINARITE.

**CUPREOUS MANGANESE.** A variety of wad or earthy manganese. (See MANGANESE, OXIDES OF, and WAD.)

**CUPRIC COMPOUNDS.** See COPPER (pp. 41, 55).

**CUPRICOUM.** Cu = 31.6. The radicle of the cupric compounds (p. 41).

**CUPRITE.** Native cuprous oxide (p. 70).

**CUPROPLUMBITE.** A sulphide of copper and lead from Chili, occurring in forms of the regular system, with cubic cleavage; also massive, granular. Specific gravity = 6.408 to 6.423. Hardness = 2.5. Lustre metallic. Colour blackish lead-grey. Streak black. Rather sectile and brittle. Fuses readily on charcoal before the blowpipe; yields with soda a cupreous lead-globule; melts and gives off sulphurous anhydride when heated in an open tube.

According to Plattner's analysis (Pogg. Ann. lxi. 672), it contains 64.9 per cent. lead, 19.5 copper, 0.5 silver, and 15.1 sulphur (estimated by loss), whence the formula  $2PbS.Cu^2S$ , or  $\begin{matrix} Pb^4 \\ Ccu^3 \end{matrix} S^2$ .

According to G. Ulrich (Berg. u. hüttenm. Zeitung, xviii. 221), a mineral of the same composition is found in small quantity on the M'Ilvor river in Victoria, Australia. It has the aspect of fine-grained galena. Hardness = 3.0 to 4.0, and apparently rhombohedral cleavage.

**CUPROSUM.** Ccu = 63.2. — The radicle of the cuprous compounds. (See COPPER, pp. 41, 46.)

**CURARA.** *Urari, Woorara, Woorali, Wourali.*—A resinous substance used by the Indians of South America for poisoning their arrows, and consisting, according to several authorities, of the aqueous extract of a climbing plant belonging to the genus *Strychnos*. It is a brown-black, shining, brittle, resinous mass, almost wholly soluble in water, either cold or warm; sparingly soluble in absolute, easily in aqueous, alcohol; partially soluble in ether. It has a bitter taste, neutral reaction, and when heated, burns with a yellowish-red flame, giving off vapours which have a disagreeable odour. Its chemical nature is not accurately known. Boussingault and Roulin attribute its poisonous action to the presence of a peculiar alkaloid, curarine (*q. v.*), while others ascribe its effects to the presence of strychnine.

Curara may be introduced with impunity into the alimentary canal, except in very large doses, but if introduced into a puncture in the skin, so that it may mix with the blood, its action is rapidly mortal. Humboldt states that the earth-eating Otomaks on the Orinoco are in the habit of anointing their thumb-nails with it, and that a mere scratch with such a nail is sufficient to produce fatal effects. The Indians use arrows poisoned with curara in the chase, the flesh of animals thus killed being perfectly wholesome. Curara acts chiefly on the motor nerves, the functions of which it completely arrests, while the sensorial nerves retain their activity. Death ensues from paralysis of the nerves of the respiratory organs.

From the researches of Reynoso, it appears that chlorine and bromine decompose curara, and completely neutralise its poisonous action. Iodine also acts as an antidote, though it does not completely decompose the curara. Nitric acid acts but slightly on curara, but may be useful as a caustic in cases of poisoning by that substance.

Curara has been tried, but without success, as an antidote to strychnine. It has also been tried as a remedy in cases of traumatic tetanus, and in one instance with success; in other cases, however, it has been found to produce no effect whatever. (Handw. d. Chem. ii. [3] 271).

**CURARINE.** (Roulin and Boussingault, Ann. Ch. Phys. [2] xxxix. 24.—A. de Humboldt, *ibid.* xxxix. 30.—Pelletier and Pétrou, *ibid.* xl. 213.—On the Poisonous Properties of Curarine; Pelouze and Cl. Bernard, Compt. rend. xxxi. 553.—A. Reynoso, *ibid.* xxxix. 67.—E. Pelikan, *ibid.* xlv. 507.—M. Milleroux, *ibid.* xvii. 973.)—An alkaloid existing in curara.

To prepare it, Pelletier and Pétrou treat the alcoholic extract of curara with ether, to remove fat and resin; dissolve the residue in water; precipitate the foreign matters with basic acetate of lead, and remove the excess of lead-salt with sulphuretted hydrogen; decolorise the liquid with animal charcoal; evaporate the filtrate and expel the acetic acid by adding sulphuric acid diluted with absolute alcohol; remove the alcohol by evaporation; precipitate the sulphuric acid with hydrate of barium; remove the excess of baryta by means of carbonic acid; and finally evaporate the filtered liquid to dryness.

Curarine thus prepared is a non-crystalline, yellowish, horny mass, translucent in thin fragments. It is deliquescent, and has a bitter taste. When heated, it chars,



emits an odour of burnt horn, and yields a slight sublimate. It dissolves in all proportions in water and alcohol, but is insoluble in ether and in oil of turpentine. It blues litmus paper reddened by acids, and reddens turmeric paper.

It unites with acids, forming bitter salts. The *sulphate*, *hydrochlorate*, and *acetate*, which are the only ones yet known, are uncrystallisable.

According to Pelikan, curarine exhibits with *acid chromate of potassium* and *sulphuric acid*, with *ferrocyanide of potassium* and *sulphuric acid*, and with *peroxide of lead*, the same reactions as strychnine, excepting that with curarine they are more permanent. It likewise exhibits the same deportment as strychnine when subjected to *electrolysis*, a red colour appearing in both cases at the positive pole.

The physiological action of curarine appears to be the same as that of curara. Pelikan found that 0.05 grms. of curarine introduced under the skin of a rabbit killed it in a short time. He is of opinion that there is no antidote to the poisonous action of curara and curarine.

**CURCUMA.** See TURMERIC.

**CURCUMIN.** (A. Vogel, Schw. J. xviii. 212. — Pelletier and Vogel, J. Pharm. July 1815, p. 259. — Vogel, Jun., Ann. Ch. Pharm. xlv. 297.) — A yellow resinous substance contained in turmeric root. To extract it, the pulverised root is first boiled with water to remove gummy matters, &c.; the residue then treated with boiling alcohol; the filtered alcoholic solution evaporated; the residue digested with ether; and the ethereal solution evaporated at a gentle heat. The residue consists of curcumin contaminated with a small quantity of essential oil, from which it may be freed by redissolving in alcohol, precipitating with acetate of lead, decomposing the lead-precipitate with sulphuretted hydrogen, and then treating it with boiling ether, which takes up the curcumin.

By evaporating the ethereal solution, the curcumin is obtained in thin resinous plates of the colour of cinnamon, but yellow when reduced to powder. When exposed to sunshine, it gradually loses its colour and becomes yellowish-white. It is heavier than water, and insoluble therein, but dissolves with facility in alcohol, ether, and oils both fixed and volatile. The alcoholic solution is precipitated by gelatin. Curcumin melts at 40° C., and is completely decomposed by distillation.

**CUSCONINE.** Syn. with ARICINE (i. 357).

**CUSPARIN.** A non-azotised crystallisable substance, soluble in alcohol, sparingly soluble in water, contained in the bark of the true angustura (*Cusparia febrifuga*) (Saladin, J. Chim. med. 1833, ix. 388). Herzog (Arch. Pharm. [2] xciii. 146) was not able to obtain this substance.

**CUTIN.** A peculiar modification of cellulose, contained, according to Fremy, in the epidermis of leaves, petals, and fruits, together with ordinary cellulose, albumin, pectous substances, and fat. It is especially distinguished from ordinary cellulose (i. 820) by being insoluble in ammoniacal solution of oxide of copper (*cuprammonia*). To prepare it, the epidermis of leaves, or the leaves themselves, are boiled for half an hour with weak hydrochloric acid and washed with water; the woody fibre is removed from the residue by aqueous *cuprammonia*; and the undissolved portion is treated successively with water, hydrochloric acid, weak aqueous potash, alcohol, and ether. (Fremy.)

Cutin exhibits under the microscope the aspect of an amorphous perforated film. It is very extensible, contains 73.66 per cent. C, 11.37 H, and 14.97 O, approaching in composition to the fats (Fremy). It decomposes when heated, producing fatty acids. It is not decomposed by cold *nitric acid*, but when boiled with that acid, yields all the products that are formed in like manner from the fats, especially suberic acid. It is not altered by contact with cold oil of vitriol or boiling hydrochloric acid. It is saponified by boiling concentrated aqueous *potash*, and from the soap thus formed, a liquid fatty acid may be separated, which is soluble in alcohol and ether, but appears to be different from oleic acid. Cutin is not altered by dilute aqueous *alkalis*, by *ammonia*, or by any neutral solvent. (Fremy, Compt. rend. xlviii. 669.)

According to Payen, on the other hand (Compt. rend. xlviii. 893), the epidermis of plants consists of cellulose impregnated with fats, nitrogenous bodies, and inorganic salts; he denies the existence of any peculiar constituent of it not containing nitrogen or cellulose, and regards the cutin of Fremy as a product of the transformation of cellulose by the reagents above mentioned.

**CYAMELIDE.** Insoluble *Cyanuric acid*,  $n\text{C}_2\text{N}_2\text{H}_2\text{O}_2$ . (Liebig, Pogg. Ann. xv. 561; xx. 384). A white crystalline substance polymeric with cyanic acid (perhaps  $\text{C}_2\text{N}_2\text{H}_2\text{O}_2$ ), which is produced, together with liquid cyanic acid, in the dry distillation of cyanuric acid; sometimes forms spontaneously in the aqueous solution of cyanic acid; and is obtained when certain cyanates are treated with concentrated acids; for



example, when cyanate of potassium is triturated with fuming nitric or sulphuric acid, with crystallised oxalic or tartaric acid, or with strong acetic or hydrochloric acid.

Cyamelide is tasteless, inodorous, insoluble in water both hot and cold, also in alcohol, ether, and dilute acids. When heated, it is converted into cyanic acid, which volatilises. Heated with strong sulphuric acid, it decomposes with effervescence, yielding carbonic anhydride and sulphate of ammonium. It is not altered by boiling with hydrochloric or nitric acid. It dissolves easily in potash, and the solution when evaporated yields cyanurate of potassium, a small quantity of ammonia being, however given off, arising from a secondary decomposition. Cyamelide is likewise soluble in ammonia.

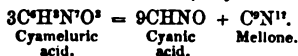
**CYAMELURIC ACID.**  $C^3H^3N^3O^3$ . An acid discovered in 1850 by Henneberg (Ann. Ch. Pharm. lxxxiii. 236), who assigned to it the formula,  $C^3H^3N^3O^3$ . Gerhardt (Compt. chim. 1850, 104) regarded it as  $C^3H^3N^3O^3$ ; but Liebig (Ann. Ch. Pharm. xcv. 281) showed that the true formula is  $C^3H^3N^3O^3$ . The acid is tribasic and may be derived from the type,  $NH^2.3HHO$ , according to which its rational formula is  $(CN^2)^3N$   
 $\begin{matrix} H^3 \\ \backslash \\ O^3 \end{matrix}$

Cyameluric acid is formed from mellone by the action of alkalis at the boiling heat, the reaction being represented, according to Liebig, by the equation:



The potassium-salt is prepared by evaporating a mixture of 1 pt. mellonide of potassium, 10 pts. potash-ley of specific gravity 1.2, and 20 pts. water at the boiling heat, the water being renewed as it evaporates, till the concentrated mass is no longer curdy, but exhibits crystals on its surface, and the liquid solidifies on cooling to a magma of needle-shaped crystals. These are washed, first with potash-ley, then with alcohol, and recrystallised from boiling water. On cooling, the cyamelurate of potassium crystallises in colourless prismatic needles having a glassy lustre. Its aqueous solution mixed with hydrochloric acid deposits cyameluric acid as a white powder, and on dissolving this in boiling water containing a few drops of hydrochloric acid, the cyameluric acid crystallises on cooling in white crystalline crusts, containing a few separate crystals in the form of prisms with pyramidal summits.

Crystallised cyameluric acid contains  $2\frac{1}{2}$  at. (16.9 per cent.) water of crystallisation its formula being  $2C^3H^3N^3O^3 + 5 aq.$ ; the whole of this water is given off at  $100^\circ C$ . The crystals dissolve in about 720 pts. water at  $17^\circ C$ ., more readily in hot water: the solution reddens litmus. The dry acid, exposed to a moderate red heat, turns yellow, gives off vapours of cyanic acid, and yields a white sublimate, probably consisting of cyanuric acid, with a yellow residue of mellone (tricyanuramide).



Cyameluric acid boiled with nitric acid yields a crystalline product, probably cyanuric acid.

**CYAMELURATES.** Cyameluric acid is tribasic, and forms three classes of salts, viz.: *neutral* or *trimetallic* =  $C^3N^3M^3O^3$ ; *dimetallic* =  $C^3N^3HM^2O^3$  and *monometallic* =  $C^3N^3H^2MO^3$ . It unites directly with bases and decomposes carbonates. Strong acids decompose the cyamelurates, separating cyameluric acid.

*Cyamelurate of Ammonium* crystallises in needles, which are very soluble in water, and fall to powder when exposed to the air, giving off ammonia and leaving an acid salt.

The *Barium-salt*,  $2C^3Ba^2N^3O^3 + aq.$ , obtained by boiling a dilute solution of the potassium-salt with excess of chloride of barium, crystallises in microscopic needles very slightly soluble in water, and giving off the greater part of their crystallisation-water at  $100^\circ C$ .

The *Cupric salt* is bluish white, granulo-crystalline, soluble in ammonia. The *Ferric salt*, precipitated from a perfectly neutral solution of ferric chloride by cyamelurate of potassium, forms a yellow bulky precipitate resembling ferric phosphate. The *Magnesium-salt* is a white crystalline precipitate insoluble in water, soluble in sal-ammoniac.

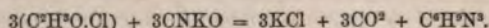
*Cyamelurates of Potassium.*—The *tripotassic-salt*,  $C^3K^3N^3O^3 + 3 aq.$ , prepared as above described, forms white shining needles often several inches long, has a strong alkaline reaction, tastes soapy at first, then bitter and irritating. It dissolves in 7.4 pts. water at  $18^\circ C$ ., and in 1 or 2 pts. of boiling water, but is insoluble in alcohol. The solution precipitates the alkalis and alkaline earths. The air-dried salt gives off 3 at.

water when left over oil of vitriol or heated to between  $100^{\circ}$  and  $120^{\circ}$  C.; at a low red heat, it melts, giving off first ammoniacal, afterwards acid vapours. The *dipotassic salt*,  $C^{\circ}K^2HN^3O^3 + 2 \text{ aq.}$ , separates from a moderately strong and slightly warmed solution of the preceding, on addition of acetic acid, in thin laminae, iridescent in sunshine. From a boiling solution, it crystallises by slow cooling in concentric groups of crystalline needles. It is somewhat more soluble in water than cyameluric acid, and has an acid reaction. The crystallisation-water is given off between  $120^{\circ}$  and  $130^{\circ}$  C. The salt when heated to redness leaves a yellow-brown fusible residue.

The *Silver-salt*,  $C^{\circ}N^{\circ}Ag^2O^3 + \text{aq.}$ , is obtained by precipitation, as a white curdy substance, forming when dry a white friable mass, sparingly soluble in dilute nitric acid. It retains a small quantity of water at  $130^{\circ}$  C. When ignited it leaves metallic silver.

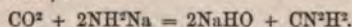
The *Sodium-salt*, obtained by decomposing carbonate of sodium with cyameluric acid, crystallises in needles, very soluble in water.

**CYAMETHINE.**  $C^{\circ}H^{\circ}N^3$ . A crystallisable organic base, polymeric with cyanide of methyl  $(CN.CH^3)$ , and homologous with cyanethine  $(C^{\circ}H^{10}N^3$ , p. 189), produced, with evolution of carbonic anhydride, by the action of chloride of acetyl on cyanate of potassium:



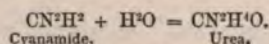
It has not been analysed, but its composition is inferred from the analogy of the reaction to that of chloride of benzoyl on cyanate of potassium, by which *cyaphenine* (q. v.) is produced. (Cloeze, Ann. Ch. Pharm. cxv. 27).

**CYANAMIDE.**  $CN^2H^2 = \begin{smallmatrix} CN \\ H^2 \end{smallmatrix} N$ . (Bineau, Ann. Ch. Phys. [2] lxxvii. 368; lxx. 251.—Cloeze and Cannizzaro, Ann. Ch. Pharm. lxxviii. 228.—W. Henke, *ibid.* cvi. 286.—Beilstein and Geuther, *ibid.* cviii. 88.—Strecker, Handw. d. Chem. ii. [3] 286.)—Bineau, by mixing dry ammonia-gas with gaseous chloride of cyanogen, obtained a product which he regarded as ammonio-chloride of cyanogen,  $CNCl.2NH^3$ . Cloeze and Cannizzaro (in 1851) showed that this substance was a mixture of sal-ammoniac and cyanamide  $(NH^4Cl + CN^2H^2)$ , and obtained the amide in the pure state by passing gaseous chloride of cyanogen into a solution of ammonia-gas in anhydrous ether. Sal-ammoniac then separates out, and the ethereal solution, evaporated over the water-bath, yields pure cyanamide. For preparing larger quantities of cyanamide, it is better to pass dry ammonia-gas and chloride of cyanogen simultaneously into anhydrous ether. Liquid chloride of cyanogen, and the bromide and iodide of cyanogen likewise yield, with ammonia-gas, mixtures of ammonium-salt and cyanamide. A compound identical in composition with cyanamide, and exhibiting similar reactions, is obtained by the action of carbonic anhydride on sodamide (Beilstein and Geuther):



Cyanamide is a white crystalline body, which melts at  $40^{\circ}$  C., often remaining liquid when cooled several degrees lower, and then solidifying suddenly by contact with a solid body. When heated to  $150^{\circ}$  C., it solidifies, with considerable evolution of heat, and is converted into the polymeric compound melamine, or cyanuramide,  $C^3N^3H^4$ .

Cyanamide is permanent in dry air and dissolves easily in water, but on evaporating the solution, it is converted into an insoluble body, probably melamine. It dissolves easily and without decomposition in alcohol and in anhydrous ether. Alkalis decompose it; with some acids, especially with nitric acid, it forms crystalline compounds. On adding a small quantity of nitric acid to its aqueous solution, nitrate of urea is produced:



A solution of cyanamide, mixed with nitrate of silver and a small quantity of ammonia, yields a flocculent yellow precipitate (? argento-cyanamide,  $CN^2Ag^2$ ), soluble in ammonia and in nitric acid. A solution of cyanamide and acetate of copper yields, on gradual addition of potash, a brown bulky copper-compound. (Beilstein and Geuther.)

Cyanamide mixed in an aqueous solution with glycol  $(C^2NH^3O^2)$ , unites with it, forming glycocyamine,  $C^3N^3H^5O^2$ , a base homologous with creatine, which separates after some days in colourless crystalline needles. (Strecker.)

*Substitution-derivatives of Cyanamide.*—These compounds, derived from cyanamide by the substitution of 1 or 2 at. of an alcohol-radicle for an equivalent quantity of hydrogen, are obtained by the action of chloride of cyanogen on ethylamine, phenylamine, &c. The ethyl and phenyl compounds are the only ones that have been studied. (See CYANETHYLAMIDE and CYANOPHENYLAMIDE.)

**Dicyano-diamide**,  $C^2N^4H^4 = \left( \begin{smallmatrix} (CN)^2 \\ H^4 \end{smallmatrix} \right) N^2$ . An aqueous solution of cyanamide left to itself for some time, or more quickly if mixed with a small quantity of ammonia, deposits a sparingly soluble substance, crystallising in broad laminae, and apparently consisting of dicyano-diamide, the molecule of which is simply that of cyanamide doubled. It unites with *nitrate of silver*, forming the compound  $C^2N^4H^4.AgNO^3$ , which crystallises in very slender needles, very soluble in boiling water, sparingly in cold water and in nitric acid. The solution of this silver-compound mixed with ammonia yields a white insoluble pulverulent precipitate consisting of  $C^2N^4H^4Ag$ .

Dicyano-diamide dissolves in *acids*, the solutions yielding by evaporation crystalline salts of the base  $C^2N^4H^4O$ . The hydrochlorate,  $C^2N^4H^4O.HCl$ , forms colourless needles, and its concentrated solution yields with *dichloride of platinum*, a crystalline precipitate,  $C^2N^4H^4O.HCl.PtCl^2$ , which crystallises from hot water in large prisms. The nitrate,  $C^2N^4H^4O.HNO^3$  (at  $120^\circ C.$ ), crystallises in colourless needles grouped in hemispheres. The oxalate  $(C^2N^4H^4O)^2.C^2H^2O^4$ , is formed on adding a warm concentrated solution of oxalic acid to a solution of dicyano-diamide, and crystallises on evaporating the liquid. Its formation is attended with copious evolution of carbonic oxide and carbonic anhydride, arising from decomposition of part of the oxalic acid added. The sulphate  $(C^2N^4H^4O)^2.H^2SO^4 + 2 aq.$  crystallises in needles which give off their water at  $100^\circ C.$  The base,  $C^2N^4H^4O$ , is obtained by heating the solution of the sulphate with carbonate of barium, and evaporating the filtrate, in colourless crystals having an alkaline reaction, easily soluble in water, slightly in alcohol. When boiled with water, it is decomposed, with evolution of ammonia, and formation of a base which appears to belong to the type  $NH^4.H.O$ , inasmuch as, when treated with hydrochloric acid, it is converted into a chloride, with elimination of 2 at. water. (Haag, Handwörterbuch, *loc. cit.*)

**TRICYANO-TRIAMIDE**,  $C^3N^6H^6$ . See CYANURAMIDE.

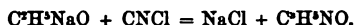
**CYANDIETHYLAMIDE**. See CYANETHYLAMIDE.

**CYANETHINE**,  $C^3H^{13}N^3$ . (Frankland and Kolbe, Chem. Soc. Qu. J. i. 69; Ann. Ch. Pharm. lxx. 288).—An organic base, polymeric with cyanide of ethyl  $(CN.C^2H^5)^3$ , and probably having the constitution of a triamide,  $N^3.(C^2H^5)^3$  (Hofmann). It is obtained by the action of potassium on that compound. Hydride of ethyl is evolved with brisk effervescence, and a yellow viscid residue is obtained, consisting of cyanide of potassium mixed with a small quantity of cyanethine, from which the cyanide of potassium may be dissolved out by cold water.\* It is difficult to account for the evolution of hydride of ethyl in this reaction, unless it be supposed that the potassium used was mixed with hydrate of potassium.

Cyanethine crystallises from boiling water in white nacreous scales. It has no smell, and very little taste, melts at  $190^\circ C.$ , and boils with partial decomposition at  $280^\circ$ . Cold water dissolves it very slightly, boiling water more freely, alcohol in all proportions. The aqueous solution has a faint alkaline reaction. Cyanethine may be boiled and even melted with potash, without alteration.

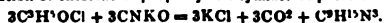
Cyanethine dissolves easily in all *acids*, forming salts which have a rough and slightly bitter taste, are soluble in water and in alcohol, and often crystallisable. The *acetate* gives off acetic acid when evaporated in vacuo, and is converted into an insoluble basic salt. The *hydrochlorate* and the *sulphate* are very soluble in water, and uncrystallisable. The *chloroplatinate*,  $C^3H^{13}N^3.HCl.PtCl^2$ , is obtained by precipitation as a reddish yellow crystalline salt, moderately soluble in alcohol, less in water, and crystallising therefrom by evaporation in large ruby-coloured octahedrons. The alcoholic solution is decomposed by evaporation, yielding chloroplatinate of ammonium. The *nitrate*,  $C^3H^{13}N^3.HNO^3$ , crystallises in large colourless prisms, which are perfectly neutral. The *oxalate* forms fine prismatic crystals.

**CYANETHOLINE**,  $C^3H^9NO$ . (Cloe, Compt. rend. xlv. 482; Ann. Ch. Pharm. cii. 354).—An organic base isomeric with cyanate of ethyl  $(CN.C^2H^5.O)$ , produced by the action of gaseous chloride of cyanogen on a solution of ethylate of sodium in absolute alcohol:



On decanting the liquid from the deposit of chloride of sodium, and distilling it in the water-bath, cyanetholine remains as a syrupy liquid of specific gravity 1.127 at  $16^\circ C.$ , which may be freed from chloride of sodium by washing with water. It has a faint odour, like that of sweet oil of wine, and a disagreeable bitter taste. It is insoluble in water, but dissolves in all proportions in alcohol and ether. It is decom-

\* The quantity of cyanethine obtained by the process above described is extremely small: it might perhaps be obtained more readily by a process analogous to that by which Cloez has obtained cyapethine (q. v.), viz. by the action of chloride of propionyl on cyanate of potassium,



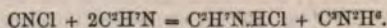


posed by distillation, leaving a carbonaceous residue. By boiling with strong potash-ley it is decomposed, with evolution of ammonia (? ethylamine). When nitric oxide is passed into a solution of the base in nitric acid, nitrogen is evolved, and a crystallisable substance, not yet examined, is deposited.

Cyanetholine dissolves in acids, forming salts which are mostly crystallisable. The *chloroplatinate* is yellow. The *nitrate* forms with nitrate of silver a double salt which separates in large crystals. The *sulphate* crystallises in small prisms when its solution is evaporated over oil of vitriol.

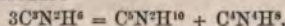
**CYANETHYLAMIDE.**  $\text{C}^{\text{N}}\text{N}^{\text{H}} = \text{C}^{\text{H}}\text{N}^{\text{H}} \left\{ \begin{smallmatrix} \text{CN} \\ \text{H} \end{smallmatrix} \right\} \text{N}$ . (Clœez and Cannizzaro, Ann.

Ch. Pharm. lxxviii. 288.)—Produced by the action of gaseous chloride of cyanogen on ethylamine :



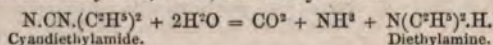
It is a weak base, uniting with concentrated acids, and forming compounds which are decomposed by water. At 180° C. it is resolved into cyandiethylamide, which distils over at that temperature, and a solid amber-coloured body, which volatilises without decomposition at 300° C. The latter is a feeble base,  $\text{C}^{\text{N}}\text{N}^{\text{H}}\text{H}$ , which forms with hydrochloric acid and dichloride of platinum, a crystalline compound, nearly insoluble in water, but easily soluble in alcohol, especially when heated, and separating in fine yellow scales on cooling.

*Cyandiethylamide*,  $\text{C}^{\text{N}}\text{N}^{\text{H}} = \left\{ \begin{smallmatrix} \text{CN} \\ (\text{C}^{\text{H}}\text{N})^2 \end{smallmatrix} \right\} \text{N}$ .—Produced as just mentioned, by the decomposition of cyanethylamide :

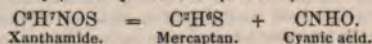


Also by passing chloride of cyanogen into a solution of diethylamine in anhydrous ether.

It is a colourless liquid which boils at 190° C., and is decomposed by acids and alkalis into carbonic anhydride, water, and diethylamine :

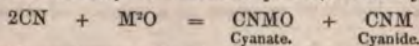


**CYANIC ACID.**  $\text{CNHO} = \left\{ \begin{smallmatrix} \text{CN} \\ \text{H} \end{smallmatrix} \right\} \text{O}$ , or  $\left\{ \begin{smallmatrix} (\text{CO})^n \\ \text{H} \end{smallmatrix} \right\} \text{N}$ . (Wöhler, Gilb. Ann. lxxi. 95; lxxiii. 15.—Pogg. Ann. i. 117; v. 335; Ann. Ch. Pharm. xlv. 351.—Liebig, Kastn. Arch. vi. 145; Schw. J. xlvi. 376; Pogg. Ann. xv. 561, 619.—Liebig and Wöhler, Pogg. Ann. xx. 369.—Baeyer, Ann. Ch. Pharm. cxiv. 156.—Brüning, *ibid.* civ. 198.)—This acid, originally distinguished by the name of *cyanous acid* (cyanuric acid being then regarded as a higher oxide of cyanogen and called *cyanic acid*), was first noticed by Vauquelin in 1818, afterwards obtained in a more definite state and examined by Wöhler in 1822. It is produced: *a*. In the free state: 1. By heating the polymeric compound, cyanuric acid,  $\text{C}^{\text{N}}\text{N}^{\text{H}}\text{O}^2$ , which then splits up into 3 atoms of cyanic acid. 2. By heating urea (cyanate of ammonium) with phosphoric anhydride to 40° C., the mixture then rising spontaneously in temperature to 130°—140°, and yielding a distillate of cyanic acid mixed with cyamelide (Liebig). 3. By the dry distillation of xanthamide (sulphocarbamate of ethyl), which then splits up into mercaptan (sulphydrate of ethyl) and cyanic acid (Debus):

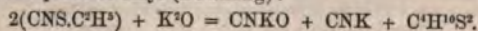


4. By heating uric acid with peroxide of manganese and sulphuric acid (Döbereiner Gilb. Ann. lxxiv. 121). 5. By heating mercuric urate to redness (Wöhler.)

*b*. In combination with bases: 1. By passing cyanogen gas into solutions of the alkalis or alkaline earths, or by heating an anhydrous alkaline carbonate to low redness in cyanogen gas, or with an anhydrous metallic cyanide, such as cyanide of mercury :



2. By fusing a cyanide or ferrocyanide of an alkali-metal in contact with the air, or with easily reducible oxides (such as oxide of lead) or with peroxides, or with small quantities of nitrates. 3. By the electrolysis of a solution of cyanide of potassium, the cyanate being then formed at the positive pole (Kolbe). 4. By igniting nitre with excess of finely divided charcoal. 5. By adding melam, ammeline, or ammeline to melting potash-hydrate as long as it dissolves (Liebig). 6. By heating sulphocyanate of ethyl with potash-ley, the products being cyanate of potassium, cyanide of potassium, and disulphide of ethyl (Brüning):



7. A solution of urea mixed with nitrate of silver and evaporated, yields cyanate of silver.

*Preparation.*—Cyanuric acid, previously dehydrated, is heated in a small retort to commencing redness, and the evolved vapour of cyanic acid is condensed in a receiver surrounded with a freezing mixture (Wöhler). The distillate thus obtained is always more or less clouded by the presence of the insoluble polymeric compound, cyamelide ( $C^3N^3H^3O^3$ ), which likewise sublimes in the neck of the retort together with unaltered cyanuric acid. The loss of product thus arising may be diminished, according to Baeyer, by heating the cyanuric acid in a tube bent at right angles, and laid in a combustion-furnace, in such a manner that the heat may reach the bend during the whole of the process, the heating being commenced at the bend and gradually extended backwards. It is best also to pass a stream of carbonic anhydride through the tube during the process.

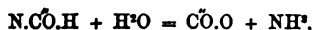
Cyanic acid cannot be separated from its salts in the ordinary way by the action of aqueous acids, because it then immediately takes up water and splits up into carbonic acid and ammonia. It may, however, be obtained by passing dry hydrochloric acid over dry cyanate of silver and collecting the evolved vapours in a cooled receiver. (Wöhler, Pogg. Ann. v. 386.)

*Properties.*—Cyanic acid is a thin, colourless liquid, which reddens litmus strongly, and has an extremely pungent odour, like that of glacial acetic acid, and somewhat like that of sulphurous acid. The vapour excites a copious flow of tears, and causes violent smarting in the hands. A drop of the liquid acid instantly produces a white blister, attended with severe pain; indeed, it is almost as dangerous to work with as strong hydrofluoric acid.

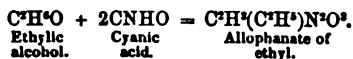
Cyanic acid may be regarded either as a hydrate of cyanogen  $\begin{matrix} \text{CN} \\ \text{H} \end{matrix} \bigg\} \text{O}$ , or as carbimide

$\begin{matrix} \text{CO} \\ \text{H} \end{matrix} \bigg\} \text{N}$ . The first of these formulæ exhibits most clearly the relations of cyanic acid to bases and to other acids; the latter, its decompositions in presence of water, the decompositions of the cyanic ethers by alkalis, &c.

*Decompositions.*—1. The liquid acid changes spontaneously into cyamelide (insoluble cyanuric acid), a substance which is polymeric with it, the change taking place the more quickly, and with greater rise of temperature, in proportion as the substance is less cooled. At  $0^\circ \text{C}$ ., the acid changes in an hour, and without explosion, into dry, hard, snow-white cyamelide; but if it be removed from the frigorific mixture, so that it may assume the ordinary temperature, it soon becomes turbid and milky, begins to boil, thickens to a pasty consistence, and becomes continually hotter, till it explodes; the paste is then scattered about, and changes completely into cyamelide. At ordinary temperatures, the conversion is complete in five minutes; it likewise takes place as quickly under increased external pressure as under the ordinary pressure. Vapour of cyanic acid mixed with an inactive gas appears to remain unchanged for a long time (Liebig and Wöhler). 2. The acid, mixed with water, splits up spontaneously in a short time, at ordinary temperatures, into 1 at. carbonic anhydride and 1 at. ammonia, the acid reaction of the liquid then changing to an alkaline reaction, and a smell of ammonia being produced. (Wöhler.)



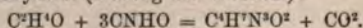
Whilst one portion of the cyanic acid is thus converted into acid carbonate of ammonium, another portion takes up the ammonia, driving out the carbonic anhydride with effervescence, and forms cyanate of ammonium, which, on evaporation, is converted into urea; and a third part of the acid is converted into cyamelide, and separates in white flakes. This decomposition is likewise attended with evolution of heat (Liebig and Wöhler). The aqueous acid, when prepared by bringing cyanic acid vapour in contact with ice, in a receiver surrounded with ice, remains nearly unaltered at the temperature of  $0^\circ$ , giving off but a few bubbles of carbonic anhydride (Liebig and Wöhler). A considerable quantity of water retards the decomposition of the acid into carbonic acid and ammonia; the presence of one of the stronger acids accelerates it, by virtue of the affinity of that acid for the ammonia (Wöhler). 3. The aqueous acid is decomposed by *sulphydric acid* (Liebig). 4. When cyanic acid vapour is passed into *methylic, ethylic, or amylalcohol*, the corresponding allophanic ethers (i. 133) are produced: *e.g.*



These ethers were originally mistaken for cyanic and cyanuric ethers (Liebig and



Wöhler). 5. With anhydrous *aldehyde*, cyanic acid forms trigenic acid, with evolution of carbonic anhydride (Liebig and Wöhler.):

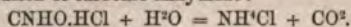


Aldehyde. Cyanic acid. Trigenic acid.

6. With *glycol*, *glycerin*, and *eugenic acid*, cyanic acid reacts in the same manner as with alcohol (Baeyer). 7. With *valeraldehyde*, it forms a compound homologous with trigenic acid. 8. When cyanic acid vapour is passed into *triethylphosphine*, no change of composition takes place in either body, but the cyanic acid is polymerised into cyanuric acid, which settles down as a white deposit. (Hofmann, Chem. Soc. Qu. J. xiii. 322.)

*Hydrochlorate of Cyanic acid*,  $CNHO.HCl$ .—When dry hydrochloric acid gas is passed through a long tube containing well-dried cyanate of potassium, great heat is produced, and a colourless liquid distils over. This reaction is always accompanied by the production of cyamelide, which remains behind on dissolving the chloride of calcium in water; and, if the cyanate of potassium be not kept cool, we obtain, instead of the above-mentioned distillate, nothing but a mixture of cyamelide and hydrochloric acid. Cyanate of silver appears to be better adapted for the preparation than the potassium-salt (Wöhler). The compound is a transparent and colourless liquid, which fumes strongly in the air, and smells very strongly of cyanic and hydrochloric acid.

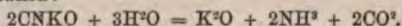
Enclosed in a sealed glass tube, it remains unaltered at  $0^\circ C.$ ; but, at ordinary temperatures, it solidifies in a few days into a crystalline mass, consisting of sal-ammoniac and cyamelide, the solidification being accompanied by the evolution of highly compressed carbonic and hydrochloric acid gases (Wöhler). The compound, heated in open vessels, is resolved into cyamelide and hydrochloric acid gas. It dissolves immediately in water, yielding a solution of sal-ammoniac, with great rise of temperature and violent evolution of carbonic anhydride:



Hence it immediately begins to effervesce when exposed to moist air, or when breathed upon, the decomposition going on till nothing remains but a solid mass of sal-ammoniac. When mixed with alcohol, it decomposes immediately, with great evolution of heat, into hydrochloric acid and *allophanic ether*. (Wöhler, Ann. Ch. Pharm. xlv. 357.)

**Cyanates.** Cyanic acid is monobasic, its salts having the formula  $CNMO$  or  $CN \begin{smallmatrix} \{ \\ M \end{smallmatrix} O$ . They are obtained, sometimes by the methods indicated for the formation of cyanic acid (p. 191); sometimes by bringing the aqueous acid in contact with the base; sometimes by precipitating an aqueous solution of cyanate of potassium or barium with a heavy metallic salt (Wöhler). In the last case, however, according to Haidlen and Fresenius, a carbonate is sometimes thrown down instead of the cyanate, *e. g.* with lead and zinc salts.

Many cyanates, as those of silver and mercury, when heated in the dry state, give off undecomposed cyanic acid, together with carbonic anhydride and nitrogen gases; others, as those of the fixed alkali-metals, remain undecomposed even at a red heat, excepting in presence of moisture, by which the salt is decomposed, at a moderate heat, into carbonate of ammonium, fixed alkaline carbonate, and a substance resembling paracyanogen; the same decomposition is produced even by repeated solution in water and evaporation:



Cyanates are decomposed by the stronger *acids*, the cyanic acid being wholly or partly decomposed by the water present, into carbonic anhydride and ammonia, so that the reaction is attended with effervescence, and the liquid, if subsequently heated with excess of potash, gives off ammonia. The pungent odour of cyanic acid is always more or less perceptible. Cyanates detonate when heated with chlorate of potassium (Wöhler). Strong sulphuric acid, dilute hydrochloric acid, and aqueous oxalic acid eliminate from cyanates scarcely any but carbonic acid, retaining the ammonia; crystallised oxalic acid, or concentrated hydrochloric acid, expels cyanic acid, which is then converted into cyamelide. Dilute sulphuric acid eliminates, together with the carbonic acid, a quantity of undecomposed cyanic acid vapour, which may be recognised by its intensely pungent odour. Some acids, as acetic acid (and likewise mineral acids, *e. g.* hydrochloric acid, according to Campbell), if added to the concentrated solution of the potassium-salt, likewise throw down crystals of acid cyanurate of potassium (Wöhler). The odour of cyanic acid is slowly, and therefore most perceptibly, evolved on dissolving cyanate of potassium in water containing cream of tartar. (Hünefeld, Schw. J. lx. 477.)



The cyanates of the alkali-metals, alkaline earth-metals, and a few others, are soluble in water. The solutions form white precipitates with nitrate of lead or silver, or with mercurous nitrate, greenish-brown with nitrate of copper, and brownish-yellow with chloride of gold (Wöhler). They do not form any precipitate with stannous or stannic chloride, ferrous or ferric chloride, or with mercuric chloride. Neither do they form prussian blue with iron-salts, on addition of sulphydric acid or sulphate of ammonium.

*Cyanates of Ammonium.*—The neutral salt  $\text{CN.NH}^4\text{O}$ , which is isomeric with carbamide(urea),  $\begin{smallmatrix} \text{CO} \\ \text{H} \end{smallmatrix} \text{N}^3$ , has not been prepared in the solid state, but may be obtained in solution by decomposing cyanate of silver with aqueous sal-ammoniac. The filtered liquid exhibits the reactions of a cyanate, but when heated or left to evaporate spontaneously, it is converted into urea.

*Basic salt.*—When vapour of cyanic acid is mixed with dry ammonia-gas, the two condense, with great evolution of heat, to a snow-white powder, very soluble in water. The solution, when evaporated, gives off ammonia, and deposits urea. The dry salt undergoes the same transformation, gradually on exposure to the air, immediately when heated; in an atmosphere of ammonia it may be preserved unaltered. (Wöhler.)

*Cyanate of Amyl.*—See CYANIC ETHERS.

*Cyanate of Barium*,  $\text{CNBaO}$ , may be obtained by passing cyanogen-gas into baryta-water, whereby cyanate and cyanide of barium are produced, decomposing the cyanide with carbonic acid, and removing the carbonate of barium by filtration (Wöhler); by mixing concentrated aqueous solutions of cyanate of potassium and acetate of barium, and adding alcohol, which throws down a precipitate of cyanate of barium (Berzelius); or most easily by heating cyanurate of barium in a retort till it melts (Berzelius). The salt crystallises in small prisms. Its aqueous solution is decomposed by boiling, into ammonia and carbonate of barium.

*Cyanate of Calcium.*—Obtained by passing cyanic acid vapour into milk of lime. It does not crystallise.

*Cyanate of Copper.*—Greenish-brown precipitate, obtained by mixing the solutions of cyanate of barium and acetate of copper.

*Cyanate of Ethyl.*—See CYANIC ETHERS.

*Cyanate of Lead*,  $\text{CNPbO}$ , is obtained by mixing the solutions of acetate of lead and cyanate of potassium, as a white precipitate composed of fine needles, and soluble in boiling water. When heated in an open vessel, it takes fire, burns with sparkling, and leaves metallic lead.

*Cyanate of Methyl.*—See CYANIC ETHERS.

*Cyanate, Mercurous.*—White precipitate, obtained by adding a solution of the barium-salt to mercurous nitrate.

*Cyanate of Naphthyl.* } —See CYANIC ETHERS.  
*Cyanate of Phenyl.* }

*Cyanate of Potassium*,  $\text{CNKO}$ .—For the various modes of formation of this salt, see page 190. It is prepared by oxidising the cyanide with metallic oxides: 1. Crude cyanide of potassium, prepared by fusing the ferrocyanide with carbonate of potassium, and containing 5 at. cyanide of potassium to 1 at. cyanate, is heated to the melting point in an earthen or iron crucible; somewhat more than three times the quantity of pulverised and gently ignited litharge is then introduced, the fused mass being stirred at the same time; the mixture is heated till the metallic lead has collected at the bottom, then poured out; and the solidified saline mass is pulverised and boiled with alcohol as long as the resulting solution continues to yield cyanate of potassium on cooling (Liebig):



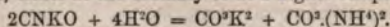
According to Clemm (Ann. Ch. Pharm. lvi. 382), the best mode of preparing cyanate of potassium is to add 15 parts of minium, by small portions at a time, to the fused and somewhat cooled, but still fluid mass of 8 pts. ferrocyanide and 3 pts. carbonate of potassium, taking care that the temperature does not rise too high. The crucible is then to be returned to the fire, and the contents stirred, poured out, and left to cool.—2. A finely-pulverised mixture of ferrocyanide of potassium and peroxide of manganese is raised to a very low red heat (if the heat be stronger, the cyanic acid is decomposed, with formation of carbonic anhydride and protoxide of manganese) (Wöhler). Or an intimate mixture of 1 pt. crystallised ferrocyanide of potassium and from 1½ to 2 pts. manganese, is formed into a cone, the point of which is set on fire by a red-hot coal, whereupon a slow combustion extends throughout the

mass (Liebig). Or better: a very finely-pulverised and intimate mixture of 2 pts. dehydrated ferrocyanide of potassium and 1 pt. manganese is heated to low redness on an iron plate, with constant stirring, the mass gradually burning with a glimmering light. The oxygen of the manganese is far from sufficient for the formation of the cyanate of potassium, but the air likewise takes part in the action; if more manganese be used, a considerable quantity of carbonate of potassium is produced (Liebig).—3. An intimate mixture of 3 pts. dehydrated ferrocyanide of potassium, 1 pt. dry carbonate of potassium, and 4 pts. very finely pounded manganese, is gently ignited in a crucible till a sample dissolved in water after cooling no longer forms Prussian blue with ferric salts. The mass, when cold, is finely pounded and boiled with 80 per cent. of alcohol (Berzelius, *Lehrbuch*).—4. A mixture of 4 pts. ferrocyanide of potassium and 3 pts. nitre, is thrown by small portions into a red-hot crucible. Strong detonation then takes place, and there remains a black mixture of undecomposed ferrocyanide, charcoal, ferric oxide, and carbonate and cyanate of potassium, the quantity of the latter amounting to 1 part. (Wöhler.)

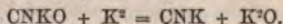
To obtain the cyanate of potassium in a purer state from the residues of these processes, they must be boiled with alcohol of the strength of 86 per cent. as long as the resulting liquid continues to yield cyanate of potassium on cooling. The alcoholic mother-liquid serves to repeat the exhaustion of the residue. The crystals must be several times washed with absolute alcohol, pressed, rapidly dried at  $100^{\circ}\text{C}.$ , or in vacuo over oil of vitriol, and preserved in a well-closed bottle, because the salt is very easily resolved by the action of moisture into carbonate of ammonium and acid carbonate of potassium. (Berzelius.)

Cyanate of potassium crystallises in small colourless laminae and needles, similar to those of chlorate of potassium. It fuses at a temperature much below redness to a transparent and colourless liquid. It is inodorous, and tastes like nitre. (Wöhler.) It dissolves readily in water, sparingly in cold hydrated alcohol, more easily in boiling hydrated alcohol; in absolute alcohol it is insoluble. (Wöhler.)

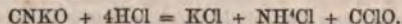
The dry salt is not decomposed by ignition; but if water be dropped upon it at that temperature, it is rapidly resolved into carbonate of potassium and carbonate of ammonium. The same change takes place when an aqueous solution of the salt is evaporated in the air, either at the ordinary or at a higher temperature (Wöhler):



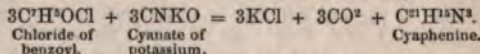
Hydrogen gas passed over the red-hot salt, abstracts all the oxygen and reduces it to cyanide of potassium; but the water thereby produced decomposes another portion of the cyanate of potassium into carbonate of potassium and carbonate of ammonium (Wöhler). Charcoal at a red heat likewise converts cyanate of potassium into cyanide (Gmelin). Potassium dissolves quite quietly in melting cyanate of potassium, forming a mixture of potash and cyanide of potassium:



Red-hot iron-filings form, with the salt, a mixture of cyanide of potassium, ferrocyanide of potassium, and protoxide of iron (Wöhler). Sulphur fuses with the salt, forming a mixture of sulphocyanate, sulphide, and sulphate of potassium (Wöhler). In this case, other decomposition-products are probably formed at the same time.—Sulphuric acid converts the melted salt into a yellow mixture of sulphide and sulphocyanate of potassium, a small quantity of sulphhydrate of ammonium being sublimed at the same time (Wöhler.) Dry hydrochloric acid gas, passed over the heated salt, produces sal-ammoniac and chloride of potassium (Wöhler); probably also phosphene is formed at the same time:



When cyanate of potassium is heated with chloride of benzoyl, carbonic anhydride is evolved, and chloride of potassium is formed, together with cyaphenine, a crystalline base polymeric with cyanide of phenyl (benzonitrile), and a small quantity of an oil boiling at  $190^{\circ}\text{C}.$ , which appears to be cyanide of phenyl:



A similar reaction takes place with chloride of acetyl, carbonic anhydride being evolved and a crystalline base produced, probably cyamethine,  $\text{C}^6\text{H}^2\text{N}^3$  (p. 290). (Cloez Ann. Ch. Pharm. cxv. 27.)

Cyanate of Silver,  $\text{CNAgO}$ , is obtained by decomposing cyanate of potassium with nitrate of silver, as a white precipitate, of specific gravity 4.004, and somewhat soluble in boiling water. Dilute nitric acid dissolves and immediately decomposes it. When heated, it melts, burns with incandescence, and leaves charcoal and metallic

silver containing nitrogen. It dissolves in ammonia, the solution yielding by evaporation, large semitransparent crystalline laminae, consisting of ammonio-cyanate of silver, or cyanate of argentammonium. When exposed to the air or immersed in water, they give up their ammonia and become opaque. (Wöhler.)

*Cyanate of Sodium* is crystallisable.

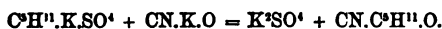
*Cyanate of Yttrium*.—Anhydrous salt, insoluble in water and in alcohol; separates after a while from a mixture of the alcoholic solutions of cyanate of potassium and an yttrium-salt. (Berlin.)

**CYANIC ETHERS.** These compounds, the cyanates of the alcohol-radicles, are obtained by distilling cyanate of potassium with ethyl-sulphate of potassium, or by the action of the iodides of the alcohol-radicles on cyanate of silver. They are volatile liquids which give, with potash and with ammonia, reactions analogous to those of cyanic acid (cyanate of hydrogen), yielding, in the first case, carbonate of potassium, and an ammonia in which 1 at. hydrogen is replaced by an alcohol-radicle, and in the second, a carbamide, or urea, in which 1 at. hydrogen is similarly replaced.

*Cyanate of Allyl*,  $C^3H^5NO = CN.C^3H^5O$ , or  $N.C\ddot{O}.C^3H^5$ . (Cahours and Hofmann, Phil. Trans. 1857, 556.)—Produced by the action of iodide of allyl on cyanate of silver. The heat produced by the reaction is sufficient to distil over nearly the whole of the volatile product. It is a transparent colourless liquid, having a pungent and intensely tear-exciting odour. It boils at  $82^\circ C$ . Vapour-density = 3.046 (exp.) = 2.88 (calc. 2 vols.) It dissolves easily, with rise of temperature, in ammonia,

and the solution when evaporated yields crystals of allyl-urea,  $\left. \begin{smallmatrix} \text{CO} \\ \text{H}^2(C^3H^5) \end{smallmatrix} \right\} N^2$ . With ethylamine, in like manner, it yields ethyl-allyl-urea. Distilled with potash it yields allylamine,  $N.H^2.C^3H^5$ .

*Cyanate of Amyl*,  $C^5H^{11}NO = CN(C^5H^{11})O$ , or  $N.C\ddot{O}.C^5H^{11}$ . (A. Wurtz, Ann. Ch. Phys. [3] xlii. 43.)—Prepared by heating 2 pts. of amylsulphate with 1 pt. cyanate of potassium:

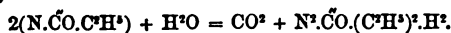


If a small quantity of mercury be added to the mixture, it may be distilled rapidly over the open fire. The distillate, if rich in cyanate of amyl, is tolerably mobile. When purified by rectification from a small quantity of a less volatile compound, it boils at about  $100^\circ C$ . With ammonia it yields amyl-urea,  $N^2.(CO).C^5H^{11}.H^2$ , and when heated with potash it yields amylamine,  $N.H^2.C^5H^{11}$ .

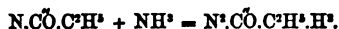
*Cyanate of Ethyl. Cyanic ether*,  $C^2H^3NO = CN.C^2H^3O$ , or  $N.C\ddot{O}.C^2H^3$ . (Wurtz, loc. cit.)—Obtained, together with cyanuric ether, by distilling cyanate of potassium with the ethylsulphate. The cyanic ether is easily separated by rectification, being very volatile, whereas the cyanuric ether, which has a triple atomic weight, does not boil till raised to a very high temperature. It may be purified by several rectifications over chloride of calcium.

Cyanate of ethyl is a transparent, colourless, very mobile liquid, of specific gravity 0.8989, and having a very high refracting power. Boils at  $60^\circ C$ . Vapour-density = 2.475 (exp.) = 2.460 (calc. 2 vols.) The vapour is very irritating, and excites a copious flow of tears.

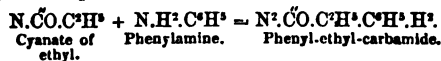
*Decompositions*.—1. Cyanate of ethyl is decomposed by water into carbonic anhydride and diethyl-carbamide:



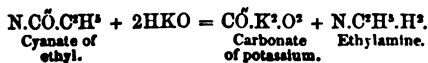
2. It dissolves in aqueous ammonia, the solution yielding by evaporation beautiful prisms of ethyl-carbamide:



With ethylamine, phenylamine, conine, &c., it yields, in like manner, carbamides in which 2 at. hydrogen are replaced by alcohol-radicles, e. g.

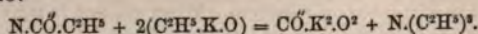


3. Boiled with potash in a sealed tube, it yields carbonate of potassium and ethylamine:

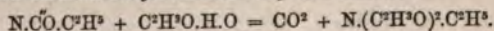




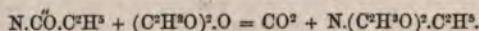
4. Heated in like manner with anhydrous *ethylate of sodium* (or *potassium*) it yields triethylamine:



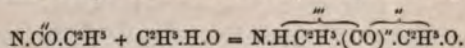
Sometimes, however, a different reaction takes place, yielding carbotriethylamine and other products (Hofmann, pp. 554, 560).—5. Cyanate of ethyl mixed with *glacial acetic acid*, yields carbonic anhydride and ethylacetamide:



6. Heated to 180° C. in a sealed tube with *acetic anhydride*, it yields ethyldiacetamide:



7. When cyanic ether is mixed with concentrated *formic acid*, violent evolution of carbonic anhydride takes place, and if the tube be then sealed and heated to 100° C., ethyl-formamide,  $\text{C}^2\text{H}^3\text{NO} = \text{N}.\text{CHO}.\text{C}^2\text{H}^3.\text{H}$ , is produced.—8. With *alcohol*, cyanate of ethyl forms ethylcarbamate of ethyl (ethyl-urethane):

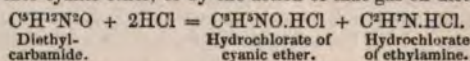


It does not act upon *ether*, even when strongly heated with it in sealed tubes for several days.—9. Cyanate of ethyl dissolves *urea* (carbamide) at a moderate heat, and the solution, heated to 100° C. for about a quarter of an hour, and then left to cool, solidifies to a crystalline mass, chiefly consisting of the compound  $\text{C}^2\text{H}^3\text{N}^2\text{O}^3$ , formed by the union of 1 at. carbamide ( $\text{CH}^3\text{N}^2\text{O}$ ) and 2 at. cyanic ether ( $\text{C}^2\text{H}^3\text{NO}$ ). This compound, which crystallises from hot water in white silky needles, and dissolves readily in alcohol,

ether, and dilute acids, is diethyl-tricarbo-tetramide,  $\left\{ \begin{smallmatrix} (\text{CO})^2 \\ \text{C}^2\text{H}^3 \\ \text{H}^1 \end{smallmatrix} \right\} \text{N}^4$ ; it contains also the elements of diethyl-cyanurate of ammonium,  $\left\{ \begin{smallmatrix} (\text{CN})^2 \\ \text{C}^2\text{H}^3 \\ \text{NH}^4 \end{smallmatrix} \right\} \text{O}^2$ ; but it

does not exhibit the characters of an ammonium-salt, not yielding diethylcyanuric acid when treated with mineral acids, or being precipitated by dichloride of platinum, or giving off ammonia when treated with cold potash, in which indeed it dissolves without decomposition; it is only when boiled with potash that it suffers decomposition, being then resolved into 2 at. ammonia, 3 at. ethylamine, and 3 at. carbonic anhydride (Hofmann, Proc. Roy. Soc. xi. 274).—10. Cyanate of ethyl, mixed with *triethylphosphine*, is gradually converted into cyanurate of ethyl; the odour of the cyanate soon disappears, and if the liquid be then treated with dilute hydrochloric acid to remove the phosphorus-base, the oil which floats on the surface quickly solidifies to a crystalline mass of cyanuric ether. (Hofmann, Chem. Soc. Qu. J. xiii. 322.)

*Hydrochlorate of Cyanic Ether*,  $\text{C}^2\text{H}^3\text{NO}.\text{HCl}$ .—Obtained by passing dry hydrochloric acid gas into cyanic ether, or by the action of that gas on diethyl-carbamide:



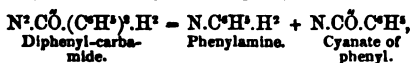
It is likewise the chief product of the action of chlorine on ethyl-carbamide. It is a liquid which has a pungent tear-exciting odour, boils at 95° C., and is immediately decomposed by water, yielding carbonic anhydride and hydrochlorate of ethylamine. (Habich and Limpricht, Ann. Ch. Pharm. cv. 395.)

*Cyanate of Methyl*,  $\text{C}^2\text{H}^3\text{NO} = \text{CN}.\text{CH}^3.\text{O}$ , or  $\text{N.C}\ddot{\text{O}}.\text{CH}^3$ . (Wurtz, loc. cit.)—Obtained by heating 2 pts. of crystallised and well dried methyl-sulphate of potassium with 1 pt. of cyanate of potassium, collecting the distillate in a well cooled receiver, and rectifying to separate the cyanate of methyl from the much less volatile cyanurate formed at the same time. It is a very volatile liquid, boiling at 90° C., and emitting highly pungent choking vapours. When sealed up in a tube, it changes in a few weeks, and often indeed in a few hours, into crystallised cyanurate of methyl. Its reactions with potash, ammonia, water, &c., are analogous to those of cyanate of ethyl.

*Cyanate of Naphthyl*,  $\text{C}^{10}\text{H}^7\text{NO} = \text{CN}.\text{C}^{10}\text{H}^7.\text{O}$ , is obtained, together with other products, by the action of phosphoric anhydride on dinaphthyl-carbamide. (V. Hall, Proc. Roy. Soc. ix. 366.)

*Cyanate of Phenyl, Aniloyanic Acid, Carbanil, Anilcarbamide, Phenyl-carbamide*,  $\text{C}^6\text{H}^5\text{NO} = \text{CN}.\text{C}^6\text{H}^5.\text{O} = \text{N.C}\ddot{\text{O}}.\text{C}^6\text{H}^5$ .—This compound, discovered by Hof-

mann in 1850 (Ann. Ch. Pharm. lxxiv. 9), was originally obtained by the dry distillation of melanoximide ( $C^{10}H^{11}N^2O^2$ ). This substance, when heated, suffers a very complicated decomposition, giving off large quantities of carbonic oxide and a small quantity of carbonic anhydride, and yielding a distillate of cyanate of phenyl mixed with diphenyl-carbamide (see MELANOXIMIDE). The latter crystallises out as the distillate cools, and on filtering the liquid and rectifying in a perfectly dry apparatus, the cyanate of phenyl is obtained pure. Cyanate of phenyl is also produced in small quantity by the dry distillation of melaniline (Hofmann, *loc. cit.*) More recently Hofmann has found that it may be obtained by the action of phosphoric anhydride, chloride of zinc, or strong hydrochloric acid, on diphenyl-carbamide, the substance then splitting up into phenylamine and cyanate of phenyl:

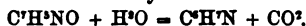


the decomposition being precisely analogous to that of carbamide (urea) into ammonia and cyanic acid. As diphenyl-carbamide is difficult to prepare, it may be replaced for

this purpose by diphenyl-oxamide,  $N.C^6H^5.O^2.(C^6H^5)^2.H^2$ , which, under the influence of phosphoric anhydride, splits up into carbonic oxide and diphenyl-carbamide. (Hofmann, Proc. Roy. Soc. ix. 274.)

Cyanate of phenyl is a thin, transparent, colourless, strongly refracting liquid, heavier than water, and boiling between  $178^\circ$  and  $180^\circ$  C. Its vapour has an extremely powerful odour of cyanogen, hydrocyanic acid, and phenylamine together, exciting a copious flow of tears, and producing a feeling of suffocation when inhaled.

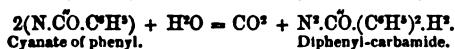
In contact with *acids* or *alkalis*, cyanate of phenyl takes up 1 at. water, and is resolved into phenylamine and carbonic anhydride:



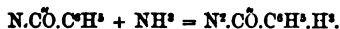
With *strong sulphuric acid*, the products are carbonic anhydride and phenyl-sulphamic acid:



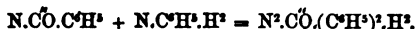
With *water*, cyanate of phenyl yields carbonic anhydride and diphenyl-carbamide:



With *ammonia*, it evolves great heat, and immediately solidifies in the form of phenyl-carbamide:



With *phenylamine*, it also becomes heated, and yields a solid mass of diphenyl-carbamide:



Other organic bases, such as *benzylamine*, *chinoline*, *cumenylamine*, &c., likewise form with cyanate of phenyl, solid products which appear to be analogous to diphenyl-carbamide. In contact with *triethylphosphine*, it is converted into solid cyanurate of phenyl. (Hofmann, Chem. Soc. Qu. J. xiii. 322.)

Cyanate of phenyl dissolves in *methylic*, *ethylic*, *amyllic*, and *phenylic alcohols*, the liquid becoming hot, and depositing, after a while, splendid crystals, which melt at the heat of boiling water, are insoluble in water, but dissolve in all proportions in alcohol and ether. The bodies thus obtained have not been analysed, but they appear to be the phenyl-carbamates of methyl, ethyl, &c. (Hofmann.)

**CYANIDES.** Compounds of cyanogen (CN, or Cy), formed on the hydrogen-type HH, or more generally nHH. The following are examples:

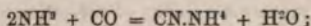
Cyanide of Hydrogen (Hydrocyanic acid)	. . . . .	H.Cy
Cyanide of Potassium	. . . . .	KCy
Cyanide of Ethyl	. . . . .	C <sup>2</sup> H <sup>5</sup> .Cy
Cyanide of Mercury*	. . . . .	Hg <sup>2</sup> .Cy <sup>2</sup>
Cyanide of Zinc and Potassium	. . . . .	$\begin{array}{c} K \\ Zn \end{array} \} Cy^2$
Cyanide of Ferricum (Ferric cyanide)	. . . . .	(Fe <sup>3</sup> ) <sup>m</sup> .Cy <sup>3</sup>
Cyanide of Potassium and Ferrosium (Ferrocyanide of Potassium)	. . . . .	$\begin{array}{c} K^4 \\ Fe^2 \end{array} \} Cy^6$
Cyanide of Potassium and Ferricum (Ferricyanide of Potassium)	. . . . .	$\begin{array}{c} K^3 \\ (Fe^3)^m \end{array} \} Cy^6$
Cyanide of Potassium and Cobalticum (Cobalticyanide of Potassium)	. . . . .	$\begin{array}{c} K^3 \\ (Co^3)^m \end{array} \} Cy^6$

\* Hg. = 200.

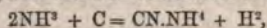


**Cyanides, Metallic.** These compounds are not found in nature ready formed, but are produced in numerous processes:

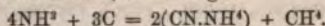
1. A few metals, potassium among the number, are converted into cyanides when heated in cyanogen gas or vapour of hydrocyanic acid, in the latter case with separation of hydrogen.—2. Cyanogen gas, passed over the heated hydrates or carbonates of the alkali-metals, forms a mixture of cyanide and cyanate of the metal; it acts in the same manner on solutions of the fixed alkalis, excepting that a brown substance like paracyanogen is also formed.—3. When nitrogen gas is passed over a mixture of charcoal and hydrate or carbonate of potassium at a bright red heat, cyanide of potassium is formed (Fownes, *J. pr. Chem.* xxvi. 412; Wöhler, *Jahresber. d. Chem.* 1850, p. 550; Rieckhen, *Ann. Ch. Pharm.* lxxix. 77; Delbruck, *ibid.* lxiv. 296.—Bunsen, *Reports of the British Association*, 1845, p. 185). Cyanide of potassium also exudes from blast-furnaces in which iron-ores are smelted with charcoal.—4. Cyanides are formed abundantly when nitrogenous organic compounds, or the nitrogenous charcoal obtained from them, are ignited with fixed alkalis. This is the principal method by which cyanides are prepared on the large scale, *e.g.* ferrocyanide of potassium, by fusing carbonate of potassium with iron filings and waste animal matter. The same reaction is used for the detection of nitrogen in organic compounds (*i.* 225). 5. Cyanides are also formed by igniting nitrates or nitrites with organic substances, either nitrogenous or non-nitrogenous: thus, nitre, fused with excess of tartrate or acetate of potassium, yields a considerable quantity of cyanide.—6. Cyanide of ammonium is formed when a mixture of ammonia-gas and carbonic oxide is passed through a red-hot tube:



also when ammonia-gas is passed over organic bodies, charcoal, or even graphite, at a red heat, the reaction being attended with elimination of hydrogen:



or sometimes according to Kuhlmann, of marsh-gas:



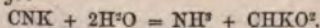
7. Cyanides are formed one from the other by double decomposition. Hydrocyanic acid converts metallic oxides into cyanides, sometimes anhydrous, as in the case of silver, but more generally hydrated. To convert an aqueous alkali (which should be free from carbonic acid) completely into cyanide, hydrocyanic acid must be added to it till it no longer precipitates sulphate of magnesium. Soluble cyanides treated with nitrate of silver yield a precipitate of cyanide of silver, and the precipitate, digested with the aqueous solution of an alkaline protosulphide, yields sulphide of silver and cyanide of the alkali-metal.

**Properties and Reactions.**—The cyanides of the alkali-metals are easily soluble in water, but most cyanides of the heavy metals are insoluble; cyanide of mercury, however, is soluble. The cyanides of the alkali-metals, cyanide of mercury, and many double cyanides containing it, are soluble in alcohol. None of the metallic cyanides are soluble in ether.

Some cyanides are crystallisable. Some are colourless, others exhibit various colours. The cyanides of the alkali-metals in the state of aqueous solution, exhibit a strong alkaline reaction, and have a bitter and alkaline taste; the solution remains alkaline, even when mixed with a very large excess of hydrocyanic acid.

Cyanide of ammonium, or hydrocyanate of ammonia, volatilises undecomposed when heated. The compounds of cyanogen with the alkali-metals sustain a red heat without decomposition, provided air and moisture be excluded. The cyanides of many of the heavy metals, *e.g.* lead, iron, cobalt, nickel, copper, &c., under these circumstances, give off all their nitrogen in the form of gas, and are converted into a compound or mixture of 1 at. metal and 1 at. carbon:  $\text{CNM} = \text{CM} + \text{N}$ .—Cyanide of mercury is resolved into metallic mercury and cyanogen gas; and cyanide of silver gives off half its cyanogen in the gaseous form, the other half, perhaps converted into paracyanogen, remaining combined with the silver.

All cyanides, when heated in the presence of water, are destroyed, those of the heavy metals generally giving off carbonic oxide, carbonic anhydride, and ammonia, and leaving the metal, together with a small quantity of charcoal. The cyanides of the alkali-metals are converted by continued boiling with water into ammoniacal gas and alkaline formates, *e.g.*:

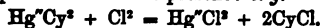


The cyanides of some of the alkali-metals, *e.g.* cyanide of potassium, when heated in contact with the air, first take up 1 at. oxygen, and are converted into cyanates ( $\text{CNKO}$ ), and these, when further heated, give off nitrogen and half the carbonic anhydride formed, and are converted into alkaline carbonates. The cyanides of the



heavy metals take fire readily when heated, yielding nitrogen, carbonic acid, and metal or oxide. Cyanides detonate by percussion with chlorate of potassium. (Johnston, Schw. J. Ivii. 379.)

*Chlorine gas* decomposes many cyanides, converting them into chlorides, and liberating cyanogen, chloride of cyanogen, either fixed or volatile, and a yellow oil, the products varying according to the presence or absence of light and water, the nature of the cyanide, and the proportion of chlorine present: *e. g.*



Chlorine, gradually introduced, converts cyanide of lead or cyanide of silver into metallic chloride and free cyanogen, which does not take up any chlorine till all cyanide is decomposed (Liebig, Pogg. Ann. xv. 571). Aqueous *chloride of lime* acts upon cyanide of silver with violent effervescence, evolving carbonic acid and nitrogen, together with a small quantity of cyanogen; but no cyanic acid is formed (Liebig). *Iodine* forms metallic iodide and cyanogen, or iodide of cyanogen. It decomposes the cyanides of the alkali-metals in the state of aqueous solution, also cyanide of silver or cyanide of copper dissolved in aqueous cyanide of potassium, forming a metallic iodide and liberating cyanogen (Gerdy, Compt. rend. xvi. 25; also J. pr. Chem. xxix. 181). With boiling aqueous cyanide of potassium, it forms iodide of potassium and iodide of cyanogen (Liebig, Ann. Ch. Pharm. l. 335). It decomposes dry cyanide of mercury, forming iodide of mercury and iodide of cyanogen.

Strong *nitric acid* decomposes all metallic cyanides, with evolution of carbonic acid, nitrogen, &c. Excess of strong *sulphuric acid* decomposes metallic cyanides at high temperatures, forming a sulphate of the metal, acid sulphate of ammonium, and carbonic oxide (Fownes):



Most cyanides, when treated with *dilute acids*, give off their cyanogen in the form of hydrocyanic acid: *e. g.*



The cyanides of the alkali-metals, which, in the state of aqueous solution, may also be regarded as hydrocyanates, are decomposed by the weakest acids, even by carbonic acid; hence their solution, if it does not contain excess of alkali, gives off hydrocyanic acid on exposure to the air, that acid being gradually expelled by the carbonic acid of the air. On the other hand, it is only the alkaline sulphhydrates and soap-solutions that are decomposed by hydrocyanic acid. (Scheele.)

The compounds of cyanogen with the heavy metals are of a more intimate nature. Some, as the cyanides of zinc and lead, give off hydrocyanic acid when treated with dilute solutions of the stronger mineral acids, such as sulphuric acid; others, as the cyanides of mercury and silver, are not decomposed, even by the strongest oxygen-acids, in the state of aqueous solution; but hydrogen-acids, such as hydrochloric and sulphydric acid, decompose them; others again, as protocyanide of gold and protocyanide of iron, withstand the action of dilute sulphuric, hydrochloric, or nitric acid, even at a boiling heat.

From the solutions of the alkaline cyanides, many heavy metallic oxides separate part of the alkali-metal, in the form of oxide, which remains dissolved, forming at the same time a heavy metallic cyanide, or a compound of that cyanide with the cyanide of the alkali-metal:



The cyanides of some metals form crystallisable compounds with the oxides of the same metal; with various metallic iodides, bromides, and chlorides; also with nitrates and chromates.

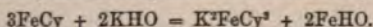
*Double Cyanides.*—Cyanides have a strong tendency to unite with one another, and form definite compounds, called *Cyanogen-salts*, or *Double Cyanides* (analogous to the iodides, bromides, and chlorides), *e. g.* cyanide of nickel and potassium,  $\text{KCy.NiCy} = \text{KNiCy}^{\text{s}}$ ; ferrocyanide of potassium,  $2\text{KCy.FeCy} = \text{K}^{\text{a}}\text{FeCy}^{\text{s}}$ . (See Table p. 197.)

The most numerous of these double salts are the compounds of the alkaline cyanides (including cyanide of ammonium,  $\text{NH}^{\text{a}}\text{Cy}$ ), with the cyanides of the heavy metals; they are formed and prepared as follows:

1. By saturating the aqueous solution of the cyanide of an alkali-metal with a heavy metallic cyanide, or, if the latter be soluble in water, adding it to the alkaline cyanide in the proportion determined by calculation.—2. By saturating the aqueous solution of the alkaline cyanide with a heavy metallic oxide or hydrate. In this case, part of the alkali-metal is separated in the form of hydrate, which remains mixed with the solution, and the heavy metal passes over to the cyanogen-compound:



3. By digesting a heavy metallic cyanide with an aqueous alkali. In this case, on the contrary, part of the heavy metal is separated in the form of hydrate:



4. By adding aqueous hydrocyanic acid to a mixture, in equivalent proportions, of a heavy metallic oxide or its carbonate, and a caustic or carbonated alkali, till the acid retains its odour even after long agitation at a gentle heat. In this case, the hydrocyanic acid drives out all the carbonic acid that may be present, and the heavy metallic oxide is dissolved.—5. By saturating with caustic potash or carbonate of potassium, the acid compound which hydrocyanic acid forms with certain heavy metallic cyanides.—6. Platinocyanides may be formed by fusing platinum with cyanide of potassium. In this case, part of the cyanide of potassium is decomposed, yielding cyanide of platinum and free potassium (which oxidises to potash), while the undecomposed portion of the cyanide of potassium unites with the cyanide of platinum formed.

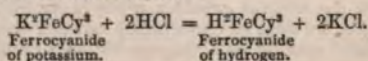
The proportions in which the heavy metallic cyanides may thus be made to unite with the cyanide of an alkali-metal, *e.g.* with cyanide of potassium, are the following:

- a. 3 at. Cyanide of potassium to 1 at. Hemicyanide of a heavy metal,  $3\text{KCy.Cu}^2\text{Cy} = \text{K}^3\text{Cu}^2\text{Cy}^4$ .
- b. 1 at. Cyanide of potassium to 1 at. Hemicyanide of a heavy metal,  $\text{KCy.Cu}^2\text{Cy}$ .
- c. 2 at. Cyanide of potassium to 1 at. Protocyanide of a heavy metal,  $2\text{KCy.FeCy}$ .
- d. 1 at. Cyanide of potassium to 1 at. Protocyanide of a heavy metal,  $\text{KCy.ZnCy}$ ;  $\text{KCy.CdCy}$ ;  $\text{KCy.NiCy}$ ;  $\text{KCy.AgCy}$ ;  $\text{KCy.AuCy}$ ;  $\text{KCy.PtCy}$ ;  $\text{KCy.PdCy}$ .
- e. 1 at. Cyanide of potassium to 2 at. Protocyanide of a heavy metal,  $\text{KCy.2FeCy}$ .
- f. 2 at. Cyanide of potassium to 1 at. Sesquicyanide of a heavy metal,  $2\text{KCy.Pt}^3\text{Cy}^3$ .
- g. 3 at. Cyanide of potassium to 1 at. Sesquicyanide of a heavy metal,  $3\text{KCy.Cr}^3\text{Cy}^3$ ;  $3\text{KCy.Mn}^3\text{Cy}^3$ ;  $3\text{KCy.Fe}^3\text{Cy}^3$ ;  $3\text{KCy.Co}^3\text{Cy}^3$ ;  $3\text{KCy.Ir}^3\text{Cy}^3$ .
- k. 1 at. Cyanide of potassium to 1 at. Tricyanide of a heavy metal,  $\text{KCy.AuCy}^3$ .

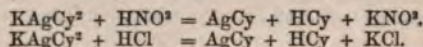
Almost all these double cyanides are crystallisable and soluble in *water*. Towards vegetable colours they are neutral or slightly alkaline, whereas the pure cyanides of the alkali-metals have a strong alkaline reaction; the double cyanides likewise emit little or no odour of hydrocyanic acid. They are also much less easily decomposable than the pure cyanides of the alkali-metals.

Both the metallic cyanides contained in these compounds behave, when ignited in a close vessel, just in the same manner as when they are ignited separately. Thus, in ferrocyanide of potassium,  $2\text{KCy.FeCy}$ , the cyanide of potassium remains undecomposed, while the cyanide of iron is resolved into nitrogen and carbide of iron.

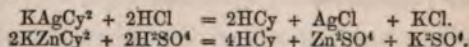
By *acids* the double cyanides are decomposed with various degrees of facility. The alkali-metal is always easily withdrawn, and its place supplied by the hydrogen of the acid. With many double cyanides, however, this change takes place without any alteration of structure in the molecule, thus:



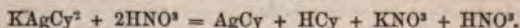
In other cases, only the alkaline cyanide is decomposed, with evolution of hydrocyanic acid, while the heavy metallic cyanide separates out; *e.g.*



If the separated cyanide is likewise decomposable by the acid used, an excess of the acid actually produces this decomposition, eliminating the whole of the cyanogen as hydrocyanic acid:



In other cases, the excess of the acid produces no further decomposition, as when cyanide of silver and potassium is acted upon by nitric acid:



Sulphydric acid precipitates the heavy metal, in the form of sulphide, from the dissolved compounds of the alkaline with the heavy cyanides, sometimes easily, as with cadmium, mercury, and silver; sometimes not at all, or but slowly and partially, as with zinc, iron, cobalt, nickel, and copper.

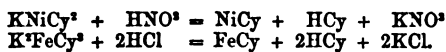
When the solution of such a compound of a cyanide of an alkali-metal with the cyanide of a heavy metal, is mixed with the salts of other heavy metals, precipitates are formed, exhibiting strong and varied colours, and generally consisting of compounds of the heavy cyanide already present, with another heavy cyanide formed by double decomposition between the cyanide of the alkali-metal and the salt of the heavy metal which has been added. Thus, ferrocyanide of potassium forms with sulphate of copper a red precipitate of ferrocyanide of copper:



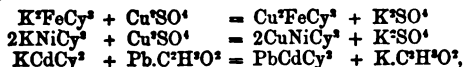
But these precipitates often retain part of the original cyanogen-salt in a state of intimate combination, so that in many cases it cannot be completely extracted even by boiling water.

On account of the different behaviour of the several double cyanides with acids, it is usual to divide them into two classes. 1. The *easily decomposable double cyanides*, which give off hydrocyanic acid when treated with a stronger acid, even in the cold. These are regarded as true double salts, that is to say, as compounds formed by the addition of two simple cyanides, e. g. cyanide of nickel and potassium,  $\text{KCy.NiCy}$ .—2. The *less easily decomposable double cyanides*, which, when treated with acids, do not evolve hydrocyanic acid, but merely exchange their alkali-metal with the hydrogen of the acid, as is the case with the double cyanides of iron, chromium, cobalt, and manganese. In these compounds, the cyanogen is usually supposed to be more intimately combined with the heavy metal, forming a compound radicle, which, like chlorine or cyanogen itself, can unite with metals, forming salts which are decomposed by acids, and yield the hydrogen-salt of the same compound radicle. Thus, the yellow cyanide of iron (ferrosium) and potassium,  $\text{K}^{\text{f}}\text{FeCy}^{\text{s}}$ , is regarded as the potassium-salt of the radicle *ferrocyanogen*,  $\text{FeCy}^{\text{s}} = \text{C}^{\text{f}}\text{N}^{\text{f}}\text{Fe}$ , usually denoted by  $\text{Cfy}$ ; hence it is called *ferrocyanide of potassium*. In like manner, the red cyanide of iron (ferricum) and potassium,  $\text{K}^{\text{s}}\text{Fe}^{\text{f}}\text{Cy}^{\text{s}} = \text{K}^{\text{s}}\text{Fe}^{\text{f}}\text{Cfy}$ , may be regarded as *ferri- or ferrid-cyanide of potassium*,  $\text{K}^{\text{s}}\text{Fe}^{\text{f}}\text{Cy}^{\text{s}}$ , or  $\text{K}^{\text{s}}\text{Cfdy}$ , a compound of potassium with *ferri- or ferrid-cyanogen*,  $\text{Fe}^{\text{f}}\text{Cy}^{\text{s}}$ . Similar compound radicles are supposed to exist in the double cyanides of chromium, cobalt, and manganese.

This view of the composition of the second class of double cyanides is convenient, when a particular class of reactions is under consideration, viz. the interchange of the alkali-metal of the double cyanide for hydrogen, or for a heavy metal; but it is by no means necessary to regard them in this way; in fact, the behaviour of a double cyanide with acids appears to depend rather upon the peculiar nature of the heavy metal contained in it than on any particular molecular arrangement. The first stage of the decomposition is the same in all cases, the alkali-metal being replaced by hydrogen; but the hydrocyanic acid thus formed remains, in some cases, combined with the heavy metallic cyanide, while in others it separates:



If now we turn our attention to the reactions which take place when these double cyanides are decomposed by *metallic salts*, instead of by the corresponding acids (hydrogen-salts), e. g.



we find that the combination or separation of the resulting cyanides is not determined by the constitution of the original double cyanide, since the components of the same double cyanide (cyanide of nickel and potassium for example), may separate when the alkali-metal is replaced by hydrogen, whereas, when it is replaced by a metal, the resulting cyanides remain united.

Neither can any difference of constitution in the two classes of double cyanides be inferred from the fact that some of these compounds, containing two heavy metals, the cyanide of nickel and copper, for example, are decomposed by acids, whereas others, as the cyanide of iron and copper, are not, this difference being due rather to the different nature of the metals present. Prussian blue, which is a ferrocyanide of iron,  $\text{Fe}^{\text{f}}\text{Cy}^{\text{s}}$ , or  $(\text{Fe}^{\text{f}})^{\text{a}}\text{Fe}^{\text{f}}\text{Cy}^{\text{s}}$ ,\* produced by the action of ferrocyanide of potassium on sesquichloride of iron, is not at all attacked by dilute acids, whereas, if one portion of the iron existed within the radicle and the rest without, the latter portion might be expected to dissolve in acids while the former remained. So likewise with the different

\*  $\text{Fe}^{\text{f}} = \text{Fe}^{\text{s}}$ .



behaviour of double cyanides with sulphydric acid; it is the nature of the heavy metal that determines whether decomposition shall take place or not, rather than any peculiarity of molecular constitution; thus, cadmium, mercury, and silver are easily precipitated by sulphydric acid from solutions of their double cyanides; nickel, copper, zinc, and manganese slowly and very imperfectly; iron and cobalt not at all.

With *alkalis*, the various double cyanides exhibit, for the most part, similar reactions. Those which contain alkali-metals are not decomposed at all by alkalis, even at the boiling heat. Those which contain only heavy metals, ferrocyanide of copper and the prussian blues for example, are decomposed in such a manner that part of the heavy metal is replaced by an alkali, so that a soluble double cyanide is formed, and a metallic oxide separated; but these decompositions often take place in such a manner as to show that no particular part of the metal is more intimately combined with the cyanogen than the rest; thus ferricyanide of iron (Turnbull's blue),  $\text{Fe}^3\text{Cy}^6$ , or  $\text{Fe}^3\text{Fe}^3\text{Cy}^6$ , yields with potash, not ferricyanide of potassium and ferrous oxide, but ferrocyanide of potassium and ferroso-ferric oxide.

*Mercuric oxide* and *mercuric sulphate* decompose all double cyanides, except the platinocyanides; thus, ferrocyanide of potassium and prussian blue are completely converted by them into cyanide of mercury, with formation of oxides or sulphates of iron.

All cyanides which give off prussic acid when treated with dilute acids, such as cyanide of potassium, cyanide of nickel and potassium, &c., are poisonous, like prussic acid itself, whereas the more stable cyanides, like ferrocyanide of potassium, are not at all poisonous.

**Cyanides of Alcohol-radicles.** *Cyanhydric or Hydrocyanic Ethers.* These compounds may be regarded either as analogous in composition to the metallic cyanides (i.e. as hydrocyanic acid having its hydrogen replaced by an alcohol-radicle), or as the *nitriles* of acid radicles containing 1 at. carbon more than the alcohol-radicle in combination with the cyanogen: thus,

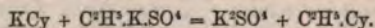
*Cyanides containing the Alcohol-radicles,  $\text{C}^n\text{H}^{2n+1}$ .*

Cyanide of Methyl, or Acetonitrile . . .	$\text{C}^2\text{H}^3\text{N} = \text{CH}^3\text{Cy}.$
Cyanide of Trichloromethyl, or Chloracetonitrile . . .	$\text{C}^2\text{Cl}^3\text{N} = \text{CCl}^3\text{Cy}.$
Cyanide of Ethyl, or Propionitrile . . .	$\text{C}^3\text{H}^5\text{N} = \text{C}^2\text{H}^3\text{Cy}.$
Cyanide of Tetryl, or Valeronitrile . . .	$\text{C}^4\text{H}^7\text{N} = \text{C}^3\text{H}^5\text{Cy}.$
Cyanide of Amyl, or Capronitrile . . .	$\text{C}^5\text{H}^{11}\text{N} = \text{C}^4\text{H}^9\text{Cy}.$
&c. &c.	

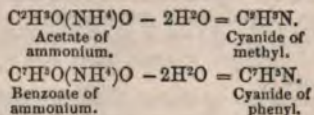
*Cyanides containing the Alcohol-radicles,  $\text{C}^n\text{H}^{2n-1}$ .*

Cyanide of Phenyl, or Benzonitrile . . .	$\text{C}^7\text{H}^5\text{N} = \text{C}^6\text{H}^5\text{Cy}.$
Cyanide of Nitrophenyl, or Nitro-benzonitrile . . .	$\text{C}^7\text{H}^4\text{N}^2\text{O}^2 = \text{C}^6\text{H}^4(\text{NO}^2)\text{Cy}.$
Cyanide of Benzyl . . .	$\text{C}^8\text{H}^7\text{N} = \text{C}^7\text{H}^7\text{Cy}.$
Cyanide of Cumenyl, or Cumonitrile . . .	$\text{C}^{10}\text{H}^{11}\text{N} = \text{C}^9\text{H}^{11}\text{Cy}.$

The cyanides of the alcohol-radicles are obtained: 1. By distilling a mixture of cyanide of potassium with an ethyl-sulphate (or homologous salt), *e.g.*



2. By the action of heat or of phosphoric anhydride on the ammonium-salts of the corresponding acids containing the radicles  $\text{C}^n\text{H}^{2n-1}\text{O}$ , or  $\text{C}^n\text{H}^{2n-1}\text{O}$ ; thus,



This last reaction gives the means of obtaining cyanides corresponding to alcohols which have not yet been formed.

The alcoholic cyanides are for the most part volatile liquids, having an odour somewhat like that of prussic acid. When treated with strong acids or alkalis, they take up water, and reproduce the ammonia-salts from which they may be formed. This action is analogous to that of cyanide of hydrogen (prussic acid), which, under the influence of acids or alkalis, yields ammonia and formic acid ( $\text{CHN} + 2\text{H}^2\text{O} = \text{NH}^3 + \text{CH}^2\text{O}^2$ ). In fact, cyanide of hydrogen (or formonitrile,  $\text{CH}_2\text{N}$ ) may be regarded as the lowest term of the series of homologous alcoholic cyanides  $\text{C}^n\text{H}^{2n-1}\text{N}$ .

**Cyanides of Acid Organic Radicles.** Two only of these compounds are known, viz the cyanides of benzoyl,  $C^6H^5O$ , and cinnamyl,  $C^9H^7O$ . They are obtained by distilling the chlorides of the corresponding acid radicles with metallic cyanides. Their reactions are analogous to those of the corresponding chlorides.

**CYANIDE OF ALLYL.**  $C^3H^3N = C^3H^3Cy$ . (Lieke, Ann. Ch. Pharm. cxii. 316.)—Obtained by heating equivalent quantities of cyanide of silver and iodide of allyl, and warming the resulting viscid oil with alcohol or ether, or distilling it with water. The product is a limpid mobile liquid, having a disagreeable pungent odour. Specific gravity = 0.794 at  $17^\circ C$ . Boils between  $96^\circ$  and  $106^\circ C$ . Somewhat soluble in water, miscible in all proportions with alcohol and ether.

**CYANIDE OF ALUMINIUM** does not appear to exist in the separate state. Hydrate of alumina does not dissolve in prussic acid, and when cyanide of potassium is added to an aluminium-salt, hydrate of alumina is precipitated free from prussic acid. A ferrocyanide of aluminium has, however, been obtained. (See CYANIDES OF IRON.)

**CYANIDE OF AMMONIUM.** *Hydrocyanate of ammonia.*  $CN^3H^4 = NH^4Cy$  =  $NH^4HCy$ .—Ammonia-gas and vapour of hydrocyanic acid unite in equal volumes, without condensation, and produce this salt. It is likewise formed, as already observed (p. 198), when ammonia-gas is passed through a red-hot tube together with carbonic oxide, or over ignited carbonaceous matter; also when charcoal in excess is ignited in a retort with sal-ammoniac and lime, or litharge. Lastly, it is sometimes formed by the action of nitric acid, nitrous acid, or nitric oxide, on organic bodies.

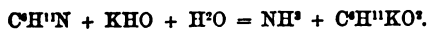
The dry salt may be prepared by heating in the water-bath 3 pts. ferrocyanide of potassium with 2 pts. sal-ammoniac, the materials being perfectly dry, and condensing the product in a receiver surrounded with ice and salt. Cyanide of mercury or cyanide of potassium may also be used instead of the ferrocyanide. Langlois prepares the salt by passing dry ammonia-gas over dry charcoal heated to redness in a porcelain tube.

Cyanide of ammonium crystallises in colourless cubes, often grouped like fern-leaves, very soluble in water and alcohol. It has a strong pungent odour of ammonia and prussic acid together. It boils at  $36^\circ C$ . The vapour is very inflammable and burns with a bluish flame, depositing carbonate of ammonia. The density of the vapour is anomalous, the molecule  $NH^4HCy$  occupying four volumes instead of two. But as hydrocyanic acid unites directly with ammonia, we may suppose that the vapour of cyanide of ammonium is a mixture of these two bodies (the molecule of each occupying two volumes), and that the salt exists only in the solid form, being decomposed at its boiling point.

Cyanide of ammonium is very instable, and gradually changes into a brown substance, *azulnic acid* (i. 480). Chlorine and bromine decompose it, forming chloride or bromide of cyanogen.

Cyanide of ammonium is highly poisonous, and yet ammonia is generally said to act as an antidote to prussic acid; according to Langlois, the beneficial action is due to the stimulating properties of the ammonia.

**CYANIDE OF AMYL.** *Capronitrile.*  $C^6H^{11}N = C^6H^{11}Cy$ . (Balard, Ann. Ch. Phys. [3] xii. 294.—Frankland and Kolbe, Ann. Ch. Pharm. lxx. 288.—Brazier and Gossleth, *ibid.* lxxv. 251.—Medlock, *ibid.* lxxix. 229.)—This compound is obtained by distilling equivalent quantities of amylsulphate and cyanide of potassium; also by the action of cyanide of potassium on chloride or oxalate of amyl. It is a very mobile oil, of specific gravity 0.8061 at  $20^\circ C$ , and vapour-density 3.335 (2 vol.). Boils at  $146^\circ C$ ; is less soluble in water than cyanide of ethyl, and dissolves in alcohol in all proportions. Boiling potash converts it into ammonia and caproate of potassium:



Potassium decomposes it, with evolution of gas, and formation of an alkaloïd resembling cyanethine.

**CYANIDE OF BARIUM,**  $BaCy$ , may be obtained in the dry state by igniting ferrocyanide of barium (Berzelius), or ferrocyanide of barium and potassium (Schulz), in a close vessel,—and in solution, by adding prussic acid to baryta-water till it no longer precipitates chloride of magnesium (Ittner). Margueritte and De Sourdaval (Compt. rend. l. 1100) prepare it on the large scale by passing air over an ignited mixture of carbonate of barium and finely divided carbon: the formation of the cyanide is said to take place with great facility. It is very soluble in water (F. and E. Rodgers), sparingly (Schulz, J. pr. Chem. lxxviii. 257), moderately soluble in alcohol, easily decomposed by carbonic acid. Heated to  $300^\circ C$  in a stream of aqueous vapour, it gives off the whole of its nitrogen in the form of ammonia. (Margueritte and De Sourdaval).

**CYANIDE OF BENZOYL.**  $C^6H^5O = C^6H^5O.CN$ . Already described (i. 568).



## 204 CYANIDE OF BENZYL—CYANIDES OF CHROMIUM.

**CYANIDE OF BENZYL.** *Cyanide of TolyI or Toluenyl.*  $C^6H^5N = C^6H^5.CN$ . (See i. 573.)

**CYANIDE OF BISMUTH** has not been obtained. Alkaline cyanides added to bismuth-salts throw down only oxide of bismuth. (Haidlen and Fresenius.)

**CYANIDE OF BUTYL.** See CYANIDE OF TETRYL.

**CYANIDE OF CACODYL.** (i. 406.)

**CYANIDE OF CADMIUM.**  $CdCy$ . Obtained in white anhydrous crystals by dissolving recently precipitated hydrate of cadmium, at a gentle heat, in hydrocyanic acid. It is permanent in the air. According to Rammelsberg, cadmium-salts are not precipitated by alkaline cyanides. According to L. Gmelin, on the contrary (Handb. vii. 426), sulphate of cadmium forms with cyanide of potassium a white precipitate, soluble in excess of the cyanide,—a result confirmed by the observations of Wittstein, of Haidlen and Fresenius, and of Schüler. (Ann. Ch. Pharm. lxxxvii. 34.)

*Cyanides of Copper and Cadmium.*—a.  $2CdCy.Cu^2Cy = Cd^2CuCy^2$ .—Recently precipitated cadmic hydrate dissolves very slowly in excess of hydrocyanic acid, but quickly, and with evolution of carbonic acid and cyanogen, on the addition of recently precipitated cupric carbonate. If the addition of the latter substance be discontinued before the oxide of cadmium is completely dissolved, there remains a lavender-blue residue, which dissolves partially in boiling water (leaving pure oxide of cadmium) and forms a liquid, which soon becomes turbid and deposits a viscid milky substance, becoming crystalline as it cools, and apparently consisting of a mixture of two different salts. But if the addition of carbonate of copper be continued till the cadmic oxide is completely dissolved, a liquid is obtained which is colourless at first, but afterwards assumes a purple-red colour, gradually in the cold, more quickly at  $20^\circ$  to  $25^\circ$  C., and after being concentrated at  $100^\circ$ , soon deposits crystals of a dingy brown-red colour. The latter compound is sparingly soluble in cold water. From the solution in a small quantity of boiling water, it separates in the form of a red tenacious mass, which gradually solidifies to a net-work of crystals; but when recrystallised from a large quantity of boiling water, it forms shining, rose-coloured, oblique rhombic prisms, which are permanent in the air, and are not decomposed at  $150^\circ$ , but at higher temperatures become opaque, fuse, and quickly decompose. (Schüler, Ann. Ch. Pharm. lxxxvii. 48.)

b.  $2CdCy.CuCy = Cd^2CuCy^2$ .—When cadmic hydrate and cupric hydrate are dissolved together in hydrocyanic acid, and the colourless solution left to evaporate in the air, colourless, shining, oblique, rhombic prisms are obtained, which at  $100^\circ$  C. give off 18.4 per cent. of their weight, and crumble to a fine mealy powder. The salt is readily decomposed by acids. Both this and the preceding have a decided alkaline reaction and a peculiar metallic taste, leaving an irritating sensation in the throat. (Schüler.)

Cyanide of cadmium forms several other double salts:

The *ferrous salt* is a yellow precipitate, obtained by mixing ferrous sulphate with cyanide of cadmium and potassium. It turns green when exposed to the air. The *lead-salt*,  $CdPb^2Cy^2 = CdCy.2PbCy$ , is a white precipitate, obtained in like manner with acetate of lead and the potassium-salt. It is decomposed by washing. The *mercury-salt*,  $2CdCy.3Hg^2Cy^2$ , obtained by dissolving cadmic hydrate and mercuric oxide in hydrocyanic acid, forms white, opaque, rectangular prisms, easily soluble in water and permanent in the air (Schüler). The *nickel-salt* is a white precipitate, soluble in excess of cyanide of cadmium and potassium, insoluble in acids. The *potassium-salt*,  $CdKCy^2$ , is obtained in shining regular octahedrons, anhydrous and permanent in the air, by evaporating a mixture of acetate of cadmium and cyanide of potassium. Weak acids separate prussic acid from it. Sulphydic acid precipitates all the cadmium. The *silver-salt* is a white precipitate, likewise soluble in excess of cyanide of cadmium and potassium.

**CYANIDE OF CALCIUM.** Obtained in aqueous solution by saturating aqueous prussic acid with slaked lime, filtering, and adding more prussic acid to the filtrate till it no longer precipitates magnesium-salts. It is decomposed by boiling, also by carbonic acid. C. Schulz prepares it in the same manner as the barium-salt, and finds that it crystallises in cubes.

**CYANIDE OF CERIUM.** Cyanide of potassium forms with cerous salts, a white gummy precipitate, which, however, quickly gives off hydrocyanic acid, and is converted into cerous hydrate. (Berenger, Ann. Ch. Pharm. xlii. 139.)

**CYANIDE OF CETYL.**  $C^{18}H^{35}.Cy$ . (See i. 840.)

**CYANIDES OF CHROMIUM.** *Chromous Cyanide*,  $CrCy$ , is obtained on mixing a solution of chromous chloride in boiled water with a solution of cyanide of



potassium, as a white precipitate, soluble in excess of the alkaline cyanide; but it oxidises very quickly during washing, and is converted into a mixture of chromic cyanide and chromic oxide.

*Chromic Cyanide*,  $\text{Cr}^2\text{Cy}^3$ , is precipitated on mixing a chromic salt with cyanide of potassium. If an aqueous solution of chromic chloride be added to a solution of cyanide of potassium, a light bluish grey precipitate is formed, insoluble in excess of the alkaline cyanide; but when the latter is added, drop by drop, to a solution of chromic chloride, the first portions of the precipitate redissolve in excess of the chromic salt; an excess of cyanide of potassium renders the precipitate persistent in the cold, but soluble on heating; and to render the precipitate quite permanent, a still larger quantity of cyanide of potassium must be added.

When a mixture of chromic hydrate, potash, and hydrocyanic acid is exposed to the air, it turns brown and yields crystals of a double cyanide of chromium and potassium, analogous in composition to ferricyanide of potassium, and capable of forming by double decomposition salts of corresponding constitution, called chromicyanides.

*Chromicyanide of Cobalt* is a blue precipitate.

*Chromicyanide of Hydrogen*, or *Hydrochromicyanic acid*,  $3\text{HCy}.\text{Cr}^2\text{Cy}^3$ , is obtained in crystals by decomposing the silver-salt suspended in water with sulphydric acid, and evaporating the filtrate in vacuo.

*Chromicyanide of Lead* is a white precipitate while moist, greyish when dry.

*Chromicyanide of Potassium*,  $3\text{KCy}.\text{Cr}^2\text{Cy}^3$ , forms crystals isomorphous with the ferricyanide, and exhibiting the faces  $\infty\text{P} . + \text{P} . - \text{P} . [\text{P}\infty]$ . The solution gives a white precipitate with zinc-salts, brick-red with ferrous salts, white with nitrate of silver; it does not precipitate nitrate of lead or ferric salts.

**CYANIDE OF CINNAMYL.**  $\text{C}^9\text{H}^7\text{NO} = \text{C}^9\text{H}^7\text{O}.\text{Cy}$  (i. 990).

**CYANIDES OF COBALT.** *Protocyanide of Cobalt*, or *Cobaltous Cyanide*, is obtained by adding cyanide of potassium to a cobaltous salt, as a flesh-coloured or light cinnamon-coloured precipitate. It dissolves in excess of the alkaline cyanide; and the solution exposed to the air is converted into a double cyanide of cobalt and potassium, analogous in composition to the ferricyanides, and yielding by double decomposition a series of salts called Cobaltcyanides, whose composition is expressed by the general formula  $3\text{MCy}.\text{Co}^2\text{Cy}^3 = \frac{\text{M}^3}{(\text{Co}^2)^3} \text{Cy}^6$ ; if we suppose these salts to contain cobalticum,  $\text{co} = \frac{2}{3} \text{Co}$ , the formula may be reduced to  $\text{MCy}.\text{coCy} = \frac{\text{M}}{\text{co}} \text{Cy}^2$ .

The *Sesquicyanide of Cobalt*, supposed to exist in these salts, is not known in the separate state.

*Cobalticyanide of Ammonium*,  $(\text{NH}^4)^3\text{Co}^2\text{Cy}^3 + \frac{1}{2} \text{aq.} = 3\text{NH}^4\text{Cy}.\text{Co}^2\text{Cy}^3 + \frac{1}{2} \text{aq.}$ , obtained by neutralising hydrocobalticyanic acid with ammonia, crystallises in rhombic tablets, very soluble in water, sparingly soluble in alcohol, and decomposing at  $230^\circ \text{C}$ .

*Cobalticyanide of Barium*,  $\text{Ba}^2\text{Co}^2\text{Cy}^3 + 12 \text{aq.}$ , obtained by dissolving carbonate of barium in hydrocobalticyanic acid, crystallises in colourless prisms, very soluble in water, insoluble in alcohol, efflorescing in warm air, and more quickly at  $100^\circ \text{C}$ .

*Cobalticyanide of Cadmium* is obtained as a brown precipitate, which afterwards turns white. It is soluble in acids and in excess of cobalticyanide of potassium.

*Cobalticyanide of Cobalt*,  $\text{Co}^2\text{Cy}^3 = 3\text{CoCy}.\text{Co}^2\text{Cy}^3$ , or  $\frac{\text{Co}}{\text{co}} \text{Cy}^2$ , analogous in composition to *Turnbull's blue* (see CYANIDES OF IRON), is prepared as follows:

1. Cobalticyanide of potassium forms with sulphate of cobalt, a light red precipitate, which may be completely freed from the potassium-salt by washing. The same precipitate is formed by adding hydrocobalticyanic acid to cobalt-salts.—2. When hydrocobalticyanic acid in the dry state is heated with strong sulphuric acid, and water added before the decomposition is complete (*vid. inf.*), cobalticyanide of cobalt is precipitated in the form of a pale red amorphous body. The product obtained by (1) contains 7 at. water, part of which it loses at  $100^\circ \text{C}$ ., turning blue at the same time, and the rest at a higher temperature. The product obtained by (2) contains only 6 at. water; when heated it gives off water, and turns blue. Cobalticyanide of cobalt is perfectly insoluble in water. Caustic potash decomposes it, separating hydrated protoxide of cobalt. Ammonia dissolves it partially, forming a reddish solution, and separating a green powder. Mercuric oxide has no action upon it. The product (2) resists the action even of strong nitric and hydrochloric acids; from (1), however, strong acids extract water and turn it blue. The anhydrous compound has a deep blue colour; in contact with moist air, it rapidly absorbs water and turns red; when water is poured upon it, combination takes place, attended with great evolution of heat. (Zwenger, *Ann. Ch. Pharm.* lxi. 172.)

**Cobalticyanide of Copper,  $3\text{CuCy}.\text{Co}^2\text{Cy}^4$ .**—The dense sky-blue precipitate which cobalticyanide of potassium forms with cupric salts (Gmelin). It is also formed by precipitating cupric salts with hydrocobalticyanic acid. It is insoluble in water and in acids; warm potash-ley separates cupric oxide from it; ammonia dissolves it completely, forming a blue solution. (Zwenger, Ann. Ch. Pharm. lxii. 170.)

**Ammonio-cobalticyanide of Copper,  $2\text{NH}^2.\text{Cu}^2\text{Co}^2\text{Cy}^4$ .**—Crystallises by slow evaporation from the ammoniacal solution of cobalticyanide of copper, in small, shining, azure-coloured, four-sided prisms, with octagonal summits; alcohol added to the ammoniacal solution throws down the compound as a blue, slightly crystalline powder of much lighter colour. The crystals are insoluble in water; when exposed to the air or heated to  $100^\circ\text{C}$ . they give off ammonia, become opaque, and assume a lighter colour. Acids withdraw the ammonia completely, leaving cobalticyanide of copper in the form of a light blue powder. When the compound is heated with potash, ammonia is given off, cupric oxide separated, and cobalticyanide of potassium left in solution. (Zwenger, loc. cit.)

**Cobalticyanide of Hydrogen, or Hydrocobalticyanic acid,  $\text{H}^2\text{Co}^2\text{Cy}^4 = 3\text{HCy}.\text{Co}^2\text{Cy}^4$ .**—Obtained (1.) by passing sulphuretted hydrogen through water in which cobalticyanide of lead [or of copper] is diffused, then filtering and evaporating to the crystalline point.—2. By decomposing the concentrated aqueous solution of cobalticyanide of potassium with a slight excess of sulphuric or nitric acid, adding absolute alcohol, and recrystallising the mass which remains after evaporation. Crystallises in deliquescent, colourless, transparent needles, having a strongly acid taste. When heated above  $100^\circ\text{C}$ . it first gives off water, then hydrocyanic acid, hydrocyanate of ammonia, and carbonate of ammonia, and at  $250^\circ\text{C}$ . leaves a blue powder, which at a higher temperature is converted into black carbide of cobalt. The aqueous solution suffers scarcely any decomposition by boiling. This acid decomposes carbonates and dissolves iron and zinc, with evolution of hydrogen. It dissolves in alcohol, but is insoluble in anhydrous ether; it is not decomposed by hydrochloric acid, fuming nitric acid, or aqua-regia. When heated with oil of vitriol, it is resolved into carbonic oxide, carbonic anhydride, sulphurous anhydride, sulphate of ammonium, and sulphate of cobalt; the addition of water before complete decomposition, gives rise to the separation of red cobalticyanide of cobalt, which, when heated, gives off water and turns blue. (Zwenger, Ann. Ch. Pharm. lxii. 147.)

**Cobalticyanide of Iron (ferrosus)** is a white precipitate obtained with ferrous sulphate and cobalticyanide of potassium. Ferric salts give no precipitate with the latter. (Zwenger.)

**Cobalticyanide of Lead,  $\text{Pb}^2\text{Co}^2\text{Cy}^4 + 2\text{aq.}$** , obtained by decomposing carbonate of lead with hydrocobalticyanic acid, crystallises in nacreous scales, very soluble in water, insoluble in alcohol. Ammonia added to the aqueous solution throws down a basic salt,  $2\text{Pb}^2\text{Co}^2\text{Cy}^4.\text{PbHO}.\text{Pb}^2\text{O}$ . (Zwenger.)

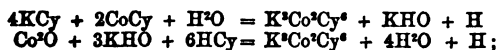
**Cobalticyanide of Manganese** is a white precipitate.

**Cobalticyanide of Mercurousum** is a white precipitate. Mercuric salts are not precipitated by cobalticyanide of potassium.

**Cobalticyanide of Nickel,  $\text{Ni}^2\text{Co}^2\text{Cy}^4$ .**—Cobalticyanide of potassium forms with sulphate of nickel, a flaky precipitate of a light sky-blue colour (Gmelin), light-green (F. and E. Rodgers). The precipitate is not attacked by boiling hydrochloric acid (Liebig).—According to Zwenger, the precipitate obtained by adding cobalticyanide of potassium to nickel-salts always contains cobalticyanide of potassium, which cannot be removed by washing. To obtain cobalticyanide of nickel in a state of purity, it is necessary to precipitate a nickel-salt with excess of hydrocobalticyanic acid. The precipitate thus obtained is gelatinous, of a light blue colour, and when exposed to the air, dries up to a transparent, greenish-blue, vitreous mass, exhibiting a conchoidal fracture. It is perfectly insoluble in water and in acids. Potash-ley decomposes it, separating hydrated oxide of nickel, but ammonia dissolves it completely. Dried at  $100^\circ\text{C}$ ., it contains 6 at. water. At a higher temperature, it gives off its water and turns grey; but the anhydrous compound, when exposed to the air, quickly absorbs a quantity of water equal to that which it has lost, and resumes its original colour. (Zwenger, Ann. Ch. Pharm. lxii. 173.)

**Ammonio-cobalticyanide of Nickel,  $2\text{NH}^2.\text{Ni}^2\text{Co}^2\text{Cy}^4 + \frac{1}{2}\text{aq.}$** —Recently precipitated cobalticyanide of nickel dissolves readily in ammonia, forming a bluish solution, which, when slowly evaporated, deposits the ammonia-compound in bluish crystalline scales. The compound may also be precipitated from the ammoniacal solution by alcohol; the precipitate is white at first, but when allowed to settle down quietly, it assumes a bluish colour. The precipitate is amorphous, and insoluble in water. Acids withdraw the ammonia, and leave cobalticyanide of nickel in the form of a light blue powder. This compound undergoes no alteration when heated in the air to  $100^\circ\text{C}$ .; at a higher temperature it takes fire, and burns away with strong intumescence. (Zwenger, loc. cit.)

*Cobalticyanide of Potassium*,  $K^2Co^2Cy^2 = 3KCy.Co^2Cy^2$ .—Obtained: 1. By treating protocyanide of cobalt with aqueous cyanide of potassium, or by gently heating carbonate of cobalt with potash and hydrocyanic acid. If the action takes place in a close vessel, it is attended with evolution of hydrogen (Gmelin):



in contact with the air, however, no evolution of hydrogen takes place, but oxygen is absorbed. The product is purified by recrystallisation. If the crystals are contaminated with cyanide or carbonate of potassium, these salts must be decomposed with acetic acid, and the solution precipitated by alcohol.

Cobalticyanide of potassium forms anhydrous flattened prisms, transparent, slightly yellow, and isomorphous with ferrocyanide of potassium. Ordinary combination  $+P. -P. \infty P \infty. [\infty P \infty]$ , the face  $-P$  sometimes predominating over  $+P$ . Twin crystals likewise occur. The salt is very soluble in water, insoluble in alcohol. When heated it melts to a dark olive-green mass, and if not in contact with the air, gives off nitrogen and cyanogen, ultimately leaving cyanide of potassium and carbide of cobalt. Sulphuric or nitric acid, added in excess to a strong solution of the salt, throws down cobalticyanide of hydrogen. The dry salt heated with strong sulphuric acid, is completely decomposed, giving off a mixture of carbonic oxide and carbonic anhydride, and leaving sulphate of cobalt mixed with sulphate of ammonium.

*Cobalticyanide of Silver*,  $Ag^2Co^2Cy^2 = 3AgCy.Co^2Cy^2$ , obtained by precipitating nitrate of silver with cobalticyanide of potassium, is a white curdy mass, anhydrous, insoluble in water and in acids, not altered by light.

It dissolves in ammonia, and the solution yields by evaporation colourless prisms of *ammonio-cobalticyanide of silver*,  $NH^2Ag^2Co^2Cy^2 + \frac{1}{2}aq.$ , or *cobalticyanide of silver and argentammonium*,  $Co^2Cy^2 \left\{ \begin{array}{l} (NH^2Ag)Cy \\ 2Ag\ Cy \end{array} \right\} + \frac{1}{2}aq.$

*Cobalticyanide of Sodium*,  $Na^2Co^2Cy^2 + 2aq.$ , prepared by saturating hydrocobalticyanic acid with carbonate of sodium, forms colourless transparent needles, very soluble in boiling water.

*Cobalticyanide of Tin (stannous)*, is a white precipitate.

*Cobalticyanide of Zinc* is a white precipitate.

**CYANIDES OF COPPER.** Cyanogen unites with copper in three different proportions, forming the cupric, cuprous, and cuproso-cupric cyanides, the last of which may be regarded as a compound of the other two.

**PROTOCYANIDE OF COPPER** or **CUPRIC CYANIDE**,  $CuCy$ , is known only in the hydrated state, and is obtained as a brown-yellow precipitate by adding cyanide of potassium, not in excess, to cold solutions of cupric salts (Scheele), or hydrocyanic acid to solution of cupric acetate (Pagenstecher). It is very unstable, decomposing spontaneously, even at ordinary temperatures, into cyanogen and hydrated cuproso-cupric cyanide; hence its properties are but little known.

According to Buignet (J. Pharm. [3] xxxv. 168), cupric cyanide is produced only when cupric sulphate is added to excess of cyanide of potassium, as a yellow-green precipitate which subsequently redissolves; if, on the contrary, the cyanide of potassium is added to excess of the cupric salt, cyanogen is evolved and cuprous cyanide is formed.

*Cuprio-cyanide of Potassium*,  $KCy.CuCy$ , separates on evaporation from the above-mentioned solution of cupric cyanide in cyanide of potassium, in rhombohedral crystals. It dissolves in  $\frac{2}{3}$  of its weight of water at  $16^\circ C.$ , and in  $\frac{1}{3}$  pt. at the boiling heat. The saturated solution boils at about  $120^\circ$ . The solution, which is colourless, is precipitated by fixed alkalis and coloured by ammonia (Baignet).

**HEMICYANIDE OF COPPER**, or **CUPROUS CYANIDE**,  $Cu^2Cy$ , or  $CcuCy$ . *Dicyanide of Copper*.—This compound is obtained in the form of a white hydrated powder by adding cyanide of potassium or hydrocyanic acid to a solution of hemichloride of copper in hydrochloric acid, or to a solution of cupric sulphate mixed with sulphurous acid. The precipitate is soluble in aqueous ammonia, dilute acids, and alkaline cyanides. It melts when heated, giving off water, and leaving a light brown-red tamed mass.

Cuprous cyanide may be obtained in anhydrous crystals, possessing considerable lustre, by suspending in water the compound of cuprous cyanide and cyanide of lead, and passing sulphydric acid gas into the liquid, taking care to avoid an excess. *Hydrocuprocyanic acid* (cyanide of cuprous and hydrogen) appears then to be formed, and if the filtered liquid be left to evaporate spontaneously, it gives off hydrocyanic acid and deposits cuprous cyanide (Wöhler, Ann. Ch. Pharm. lxxviii. 370).—According to Dauber (*ibid.* lxxiv. 216), the crystals belong to the monoclinic system, the



dominant faces being  $\infty P$ .  $\infty P\infty$ .  $\infty P$ . Inclination of  $\infty P$ :  $\infty P$  in the plane of the clinodiagonal and principal axis =  $68^\circ 32'$ ;  $\infty P$ :  $\infty P = 70^\circ 16'$ ;  $\infty P$ :  $\infty P\infty = 53^\circ 10'$ . Ratio of orthodiagonal to clinodiagonal =  $0.5453 : 1$ . Cleavage perfect, parallel to  $\infty P$ .

Cuprous cyanide unites with the cyanides of the alkali-metals, forming colourless salts, which may be called cuproso-cyanides, from which acids, added to their solutions, precipitate cuprous cyanide in thick white flakes with evolution of hydrocyanic acid.

*Cuprosocyanide of Ammonium*,  $NH_4Cu^2Cy^2$ , or  $NH_4Cy.CuCy$ .—If in the preparation of diammoniacal cuproso-cupric cyanide (p. 209), the passage of the gas be continued after the needles of the green cyanide have formed, these crystals first redissolve, after which the liquid gradually loses its colour. When concentrated and left to cool slowly, it deposits beautiful, colourless, prismatic needles of cuprosocyanide of ammonium. This salt is but sparingly soluble in water, and decomposes when continuously boiled therein. At  $100^\circ C$ , it gives off cyanide of ammonium, and at a temperature a little above, is rapidly converted into cuprous cyanide. (Dufau, Compt. rend. xxxvi. 1099.)

*Cuprosocyanide of Barium*.—When aqueous hydrocyanic acid is poured upon a mixture of carbonate of copper and hydrate of barium, the whole dissolves with brisk effervescence, forming a crimson solution, which leaves a colourless residue when evaporated. Water poured upon the residue dissolves out the colourless double cyanide, leaving a residue of carbonate of barium. (Meillet.)

*Cuprosocyanide of Bismuth*.—Cuprosocyanide of potassium *a* (p. 210) forms, with bismuth-salts, a yellowish-white precipitate, which dissolves in acids with evolution of hydrocyanic acid. (Ittner.)

*Cuprosocyanide of Cadmium*.—Cyanide of cadmium and potassium, added to solution of sulphate of copper, throws down a brownish-white precipitate, with evolution of cyanogen gas. (Rammelsberg.)

*Cuprosocyanide of Copper*, or *Cuproso-cupric Cyanide*,  $Cu^2Cy^2 = CuCy.Cu^2Cy = \begin{smallmatrix} Cu \\ Cu \end{smallmatrix} \} Cy^2$ .—The brownish-yellow hydrated cupric cyanide precipitated by cyanide of potassium from cold solutions of cupric salts (p. 207) gradually gives off cyanogen, and is converted into cuproso-cupric cyanide (Wöhler, Gmelin). The same compound is obtained by precipitating a cupric salt with cuprosocyanide of potassium (Rammelsberg). When washed and dried at ordinary temperatures, it forms siskin-green crystalline granules, or transparent prisms, having a strong lustre.

According to Dufau (Compt. rend. xxxvi. 1099), cuprous and cupric cyanide form two compounds, one having the composition just given, the other containing 2 at. cuprous to 1 at. cupric cyanide.

*a*. Dufau prepares the preceding compound by passing into a tolerably dilute solution of a cupric salt, a solution equally dilute of cyanide of potassium or hydrocyanic acid, in such proportion as to leave a considerable quantity of the copper-salt undecomposed;—or by passing a stream of hydrocyanic acid vapour into water in which cupric oxide is suspended. The precipitate formed is yellow at first, but rapidly becomes green, and gives off a considerable quantity of cyanogen. The green precipitate, which has a crystalline aspect, contains  $\frac{1}{2}$  at. water, so that its formula is  $Cu^2Cy^2 + \frac{1}{2} aq$ . At  $100^\circ C$ , it gives off water without decomposing, but at higher temperatures it gives off cyanogen, and is converted into cuprous cyanide. Acids separate white cuprous cyanide from it, producing at the same time a cupric salt, and eliminating hydrocyanic acid. Caustic potash transforms it into cuprosocyanide of potassium and cupric oxide. Ammonia dissolves it very easily, forming a blue liquid, which, by spontaneous evaporation deposits beautiful green needles of diammoniacal cuproso-cupric cyanide (p. 209).—It dissolves very readily in aqueous cyanide of potassium, forming a colourless or slightly bluish liquid, which soon changes to a crystalline mass, having a nacreous aspect, and consisting of cuprosocyanide of potassium; its formation is attended with evolution of cyanogen.

*b*.  $2Cu^2Cy.CuCy + \frac{1}{2} aq. = \begin{smallmatrix} Cu \\ Cu \end{smallmatrix} \} Cy^2 + \frac{1}{2} aq$ .—When a cupric salt is precipitated by a moderately concentrated solution of cyanide of potassium added in sufficient quantity to throw down nearly all the copper, an amorphous powder is obtained of an olive-yellow colour, and a large quantity of cyanogen is given off: the precipitate has the composition above stated.—Both this compound and the preceding (*a*) are very instable, sometimes decomposing spontaneously, sometimes on the slightest rise of temperature, and, especially in presence of a large excess of hydrocyanic acid, giving off cyanogen, and leaving cuprous cyanide. (Dufau.)

*Ammoniacal Cuproso-cupric Cyanide*,  $NH_4.Cu^2Cy.CuCy. + \frac{1}{2} aq. = \begin{smallmatrix} NH_4Cu \\ Cu \end{smallmatrix} \} Cy^2 + \frac{1}{2} aq$ .

—When a solution of cyanide of ammonium is mixed with a cupric salt, a considerable quantity of cyanogen is disengaged, and a bluish-green precipitate is formed containing ammonia, and having the composition just stated. — Bluish green amorphous powder, slightly soluble in cold water, to which it imparts a faint blue colour; when boiled in water, it gives off ammonia and is resolved into cuprocyanide of ammonium, which remains in solution, and cuprous cyanide, which is precipitated. — The cuprous cyanide obtained in this and in certain similar reactions has more or less of a brown colour, but is identical in composition with the white cyanide. The compound is permanent in the air at ordinary temperatures, but gives off water and ammonia at 100° C.; a heat somewhat greater converts it rapidly into cuprous cyanide. (Dufau.)

*Diammoniacal Cuproso-cupric Cyanide*,  $2\text{NH}^3\cdot\text{Cu}^2\text{Cy}\cdot\text{CuCy} = \frac{\text{NH}^3\text{Cu}}{\text{NH}^3\text{Ccu}} \left\{ \text{Cy}^2 \right\}$ . — 1. The preceding compound dissolves readily in ammonia, forming a sky-blue liquid, which by spontaneous evaporation deposits beautiful green needles, having the composition just stated. — 2. A more convenient method of obtaining this compound is to pass a stream of hydrocyanic acid vapour into ammonia containing cupric oxide in suspension. The oxide of copper dissolves at first under the influence of the hydrocyanic acid; but, after a while, small brilliant green needles appear in the liquid, and increase rapidly in quantity; the operation is then to be stopped, and the liquid left to cool, whereupon it deposits another crop of the green needles. — 3. This salt is also formed by dissolving cuprous cyanide in ammonia. The solution remains colourless if protected from the air, but, if oxygen has access to it, in ever so small a quantity, it rapidly turns blue, and when evaporated, deposits the green needles of the diammoniacal salt. — Diammoniacal cuprosocupric cyanide forms beautiful green prismatic needles, having a metallic lustre; it is unalterable in the air, insoluble in water, and exhibits with various reagents the same actions as cuprosocupric cyanide and the monammoniacal compound. (Dufau.)

*Triammoniacal Cuproso-cupric Cyanide*,  $3\text{NH}^3\cdot\text{Cu}^2\text{Cy}\cdot\text{CuCy} = \frac{\text{NH}^3\text{AmCu}}{\text{NH}^3\text{Ccu}} \left\{ \text{Cy}^2 \right\}$ . — The diammoniacal compound dissolves readily in warm aqueous ammonia; and if the ammonia be constantly kept in excess by passing a stream of ammoniacal gas into the liquid, the solution, when afterwards left to cool, deposits, either prismatic needles or crystalline plates of a fine blue colour. — This salt, when exposed to the air, gives off ammonia and turns green. It may also be prepared from cuprosocupric cyanide, or the monammoniacal compound. (Dufau.)

*Diammoniacal Dicroso-cupric Cyanide*,  $2\text{NH}^3\cdot\text{CuCy}\cdot 2\text{Cu}^2\text{Cy} = \frac{\text{NH}^3\text{Cu}}{\text{NH}^3\text{Ccu}} \left\{ \text{Cy}^3 \right\}$ . —

When an ammoniacal solution of cupric oxide is poured into aqueous hydrocyanic acid, till the odour of ammonia decidedly predominates, the slightly yellow liquid then heated to the boiling point, the heat kept up, and the gradual addition of the ammoniacal copper-solution continued till its dark blue colour no longer disappears, micaceous crystalline laminae make their appearance after a while. If the liquid be then filtered, it yields, on cooling, green rectangular laminae of remarkable lustre. They have a composition denoted by the preceding formula together with 1 at. water. On heating them with equal volumes of solution of caustic ammonia and carbonate of ammonium not too dilute, a blue solution is obtained, which, after boiling for an hour, deposits shining blue laminae of the anhydrous compound. The green laminae also turn blue when treated with the fixed alkalis or their carbonates, even in the cold.

The compound is quite insoluble in cold water, and is decomposed by boiling water, with formation of a brown substance. Dilute acids separate from it white cuprous cyanide, which dissolves on boiling, with evolution of hydrocyanic acid. (Hilkenkamp, Ann. Ch. Pharm. xcvi. 218.)

Monthiers (J. Pharm. [3] xi. 257), by precipitating cupric sulphate with cyanide of cuprous and ammonium, obtained a yellow precipitate, to which he assigned the formula  $\text{NH}^3\cdot\text{CuCy}\cdot 2\text{Cu}^2\text{Cy}\cdot\text{HO}$ .

*Cuprocyanide of Iron*. — *a*. Cuprocyanide of potassium, *a*, forms, with ferric salts, a greenish yellow precipitate, from which acids dissolve out cuprous cyanide, leaving a residue of protocyanide of iron (Ittner). The precipitate is white, but turns yellow when exposed to the air, the surface becoming yellowish green (Rammelsberg). — *b*. Cuprocyanide of potassium *c* forms a yellow precipitate, which turns greenish on exposure to the air (Rammelsberg); according to F. & E. Rodgers, the precipitate is white. With ferrous sulphate free from ferric oxide, no precipitate is formed (Gmelin). For the other double cyanides of copper and iron, see CYANIDES OF IRON.



*Cuprosocyanide of Lead.*—*a.* The potassium-salt forms, with lead-salts, a whitish green precipitate (white, according to Rammelsberg), which dissolves in acids with evolution of hydrocyanic acid (Ittner).—*b.* The copper-salt *b* precipitates lead-salts in fine, white, curdy flakes. (Gmelin.)

*Cuprosocyanide of Manganese.*—*a.* Cuprosocyanide of potassium *a* forms with manganeous salts a yellowish white precipitate, which dissolves in acids with evolution of hydrocyanic acid (Ittner).—*b.* The potassium-salt *c* forms a white precipitate with manganeous salts. (Gmelin.)

*Cuprosocyanide of Potassium.*—Cuprous cyanide forms three compounds with cyanide of potassium.

*a.*  $\text{KCy.Cu}^2\text{Cy} = \frac{\text{K}}{\text{Cu}} \left\{ \text{Cy}^2 \right\}$ .—This salt was discovered by Ittner, and further investigated by Leopold Gmelin and Rammelsberg.

*Preparation.*—1. Cupric hydrate or cuproso-cupric cyanide, is dissolved in aqueous cyanide of potassium, and the filtrate evaporated to the crystallising point (Ittner). Monthiers pours excess of potash on hydrated cupric oxide, and adds hydrocyanic acid till the hydrate is dissolved, and the liquid becomes quite colourless. To obtain a perfectly white salt, he avoids the application of heat.—2. Cuprous cyanide is precipitated by cyanide of potassium from the solution of cuprous chloride in hydrochloric acid, and potash added to the liquid till it reddens turmeric, then hydrocyanic acid till its odour becomes permanent, then potash again, and so on alternately; the residual white powder is then dissolved by adding a large quantity of water and boiling, and the liquid is evaporated and cooled. The salt *a* crystallises out first, afterwards the more soluble salt *b* (Gmelin).—3. This compound may also be obtained by adding cyanide of potassium to the aqueous solution of acetate of copper till the precipitate which forms at first is redissolved. The solution, which is formed with evolution of cyanogen, assumes at first a purple-red colour, but afterwards on further addition of cyanide of potassium and heating, turns yellow (Rammelsberg).—The solution, whether prepared according to 1, 2, or 3, yields on evaporation or cooling, first, a comparatively small quantity of the crystallised salt *a*, and then, by further evaporation and cooling, a larger quantity of the crystals *c*. (Rammelsberg.)

The salt forms transparent monoclinic crystals, exhibiting the faces  $\text{oP} . +2\text{P}\infty . -2\text{P}\infty . \infty\text{P} . -\text{P} . [\text{P}\infty]$ . The crystals are often much elongated in the direction of the orthodiagonal. Inclination of  $\infty\text{P} : \infty\text{P}$  in the clinodiagonal section =  $94^\circ 30'$ ;  $\text{oP} : -\text{P} = 131^\circ 54'$ ;  $\text{oP} : -2\text{P}\infty = 126^\circ 13'$ ;  $\text{oP} : [\text{P}\infty] = 136^\circ 46'$ . Inclination of clinodiagonal to principal axis =  $77^\circ 8'$  (Rammelsberg, Pogg. Ann. cvi. 491). The crystals are pale yellow according to Ittner and Gmelin, but colourless according to Rammelsberg, who regards the colouring as incidental; also according to Meillet (J. Pharm.[3] iii. 443) and Monthiers (*ibid.* xi. 255). Taste bitter and metallic.

The crystals, when heated, give off a small quantity of water [probably only hygroscopic], become white and opaque, and afterwards fuse to a transparent liquid, pale blue by transmitted light, but having fine brown-red particles floating in it, which impart a brown-red colour to it by reflected light; no further decomposition ensues at a moderate red heat (Gmelin). These brown-red particles, which separate from the originally colourless liquid, consist of very finely divided copper, whence also proceeds the blue colour which the liquid afterwards exhibits by transmitted light (Rammelsberg). Sulphuretted hydrogen passed through the aqueous solution, throws down but a small quantity of copper, even after a long time (Ittner, Rammelsberg). The stronger acids added in small quantity throw down white cuprous cyanide and eliminate hydrocyanic acid (Gmelin). The same effect is produced by the salts of ferric and stannic oxide, excepting that the hydrates of these oxides are at the same time precipitated (Ittner). Mercuric salts throw down cupric [? cuprous] cyanide, with formation of cyanide of mercury and a potassium-salt. Alkalis have no action on this compound (Ittner.) The crystals dissolve sparingly in water, with partial separation of cuprous cyanide, whereby they become opaque, and afterwards crumble to a white powder. The solution when evaporated first yields crystals of the salt *a*, then of *c*; the former is therefore rendered soluble in water only through the medium of the latter. (Rammelsberg.)

*b.*  $2\text{KCy.3Cu}^2\text{Cy} = \frac{\text{K}^2}{\text{Cu}^3} \left\{ \text{Cy}^3 \right\}$ .—Formed by the action of potash on cuprous cyanide. (Rammelsberg, Pogg. Ann. lxiv. 65.)

*c.*  $3\text{KCy.Cu}^2\text{Cy} = \frac{\text{K}^3}{\text{Cu}} \left\{ \text{Cy}^3 \right\}$ .—Discovered by Gmelin, more minutely examined by Rammelsberg. Prepared in the same manner as the salt *a*. In some cases, the salt *a* crystallises first from the liquid, and afterwards the salt *b*; or, if the quantity of cyanide of potassium present be considerable, the salt *b* crystallises out alone. According to Prince Bagration (J. pr. Chem. xxx. 367), copper dissolves in aqueous



cyanide or ferrocyanide of potassium, and in this reaction the same salt is produced together with free potash.

This salt forms colourless, transparent, rhombic prisms, truncated on the lateral edges, and having 6-sided summits (Gmelin). Permanent in the air (Rammelsberg); acquires a bluish white tint after long keeping (Gmelin). The crystals decrepitate when heated, and at a temperature much below redness they fuse without loss of water, and form a liquid which is likewise blue by transmitted, and brown-red by reflected light, and does not undergo any further decomposition at a moderate red heat; on cooling, it solidifies into a mass coloured reddish white by admixed particles of copper. Small quantities of the stronger acids precipitate cuprous cyanide from the solution, and liberate hydrocyanic acid (Gmelin). A similar effect is produced by ferric salts, a precipitate of hydrated ferric oxide being, however, formed at the same time (Rammelsberg). Mercurous nitrate forms a green precipitate (Gmelin). The salt dissolves readily in water, and its warm concentrated solution takes up a considerable quantity of the salt *a*, so that, as it cools, crystals of *a* separate out (Rammelsberg). The solution of the salt *c* forms a pale yellow precipitate with cupric salts (Gmelin, F. & E. Rodgers). This precipitate should be  $\text{Cu}^+\text{Cy}^+$  or  $\text{Cu}^+\text{CcuCy}^+$ .

This salt forms colourless, transparent, monoclinic prisms, exhibiting the faces  $\infty\text{P}$ .  $\text{oP}$ .  $-\text{P}$ .  $[2\text{P}\infty]$ , with the inclinations  $\infty\text{P} : \infty\text{P}$  in the clinodiagonal principal section =  $102^\circ 32'$ ;  $\text{oP} : \infty\text{P}$  =  $102^\circ 10'$ ;  $\text{oP} : -\text{P}$  =  $142^\circ 59'$ ;  $\text{oP} : [2\text{P}\infty]$  =  $130^\circ 57'$ .

*Cuproso-cyanide of Sodium*.—Formed by precipitating the solution of the corresponding barium-salt with an equivalent quantity of sulphate of sodium. On evaporating the filtrate, it remains in the form of small needles permanent in the air. (Meillet, J. Pharm. [3] iii. 413.)

*Cuproso-cyanide of Uranyl*.—The potassium-salt *c* added to uranic chloride throws down a pale yellow powder. (Gmelin.)

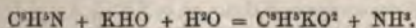
*Cuproso-cyanide of Zinc*.—The potassium-salt *a* forms with zinc-salts a white precipitate, which dissolves in acids with separation of prussic acid (Ittner). The potassium-salt *c* forms curdy white flakes. (Gmelin.)

**CYANIDE OF CUMENYL.** See CUMONITRILE (p. 283).

**CYANIDE OF ETHYL.** *Propionitrile, Metacetonitrile, Hydrocyanic ether*,  $\text{C}^2\text{H}^3\text{N} = \text{C}^2\text{H}^3\text{Cy}$ .—This compound was discovered by Pelouze in 1834 (Ann. Ch. Pharm. x. 249), further examined by Frankland and Kolbe (*ibid.* lxx. 269, 288; Chem. Soc. Mem. iii. 386; Chem. Soc. Qu. J. i. 60), and by Dumas, Malaguti and Leblanc, Ann. Ch. Pharm. lxxiv. 329). It is obtained; 1. By distilling cyanide of potassium with ethylsulphate of potassium or barium, the distillate being purified by washing with water, drying over chloride of calcium, and rectification; but the preparation by this method is attended with the evolution of an intolerable odour, arising from a small quantity of a cyanogen-compound not yet examined, and the purification is very difficult.—2. By distilling pulverised cyanide of potassium with oxalate of ethyl (Löwig).—3. By distilling cyanide of potassium with iodide of ethyl mixed with four times its volume of alcohol, the condensing apparatus being so arranged that the distilled liquid may continually run back again, till, on being tested, it shows no trace of iodine; the contents of the retort are then distilled to dryness (Williamson, Phil. Mag. [4] vi. 205). According to Buckton and Hofmann (Chem. Soc. Qu. J. ix. 250), the cyanide of ethyl thus obtained contains a considerable quantity of alcohol, from which it cannot be freed by fractional distillation; and to obtain it pure it must first be converted into propionate of potassium by the action of caustic potash (*vid. inf.*), this salt freed from alcohol by distillation, then converted into propionic ether (by heating it with alcohol and sulphuric acid),—the ether converted into propionamide ( $\text{N.H}^2.\text{C}^2\text{H}^3\text{O} = \text{C}^2\text{H}^3\text{NO}$ ) by the action of ammonia under pressure,—and the propionamide into propionitrile (cyanide of ethyl) by the action of phosphoric anhydride. Buckton and Hofmann, however, regarded this as the best method of obtaining pure cyanide of ethyl.

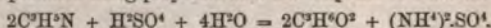
Cyanide of ethyl is a colourless liquid, of specific gravity 0.78 (Pelouze), 0.7889 at  $12.6^\circ\text{C}$ . (Frankland and Kolbe). It boils at  $82^\circ\text{C}$ . (Pelouze), at  $88^\circ$  (Frankland and Kolbe). It has a strong alliaceous odour, and is very poisonous (Pelouze). It is very soluble in water (Pelouze), moderately soluble, but separates on the addition of common salt (Frankland and Kolbe). It mixes in all proportions with alcohol and ether.

Cyanide of ethyl cohobated with aqueous potash is converted into propionate of potassium, with evolution of ammonia:

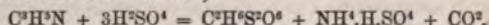


## 212 CYANIDE OF ETHYLENE—CYANIDES OF GOLD.

A similar decomposition is produced by *dilute sulphuric acid* (1 pt. strong acid to 2 pts. water), the products being propionic acid and sulphate of ammonium:



According to E. Meyer (J. pr. Chem. lxxvii. 147), sulphate of ethylamine is likewise formed. Heated with *fuming sulphuric acid*, it yields disulphethotic acid,  $\text{C}^2\text{H}^2\text{S}^2\text{O}^6$ , together with acid sulphate of ammonium and carbonic anhydride (Buckton and Hofmann (Chem. Soc. Qu. J. ix. 250):



Cyanide of ethyl, treated with potassium at ordinary temperatures, is partly decomposed, yielding cyanide of potassium and hydride of ethyl, and partly polymerised into cyanethine,  $\text{C}^3\text{H}^{12}\text{N}^3$  (Frankland and Kolbe). The formation of hydride of ethyl in this reaction must be due, either to the presence of water or alcohol in the cyanide of ethyl, or to the resolution of the liberated ethyl into hydride of ethyl and ethylene.

*Cyanide of Ethyl and Silver.*—When iodide of ethyl and cyanide of silver in equivalent quantities are heated together to  $100^\circ\text{C}$ . in a sealed glass tube, this compound is obtained as a viscid oil, which solidifies in the crystalline state on cooling. It is also obtained in fine shining crystals on heating to  $100^\circ\text{C}$ . a mixture of iodide of ethyl, cyanide of silver, and water. It does not yield pure cyanide of ethyl by dry distillation, but when distilled with water, or with potash, it yields a distillate which smells of cyanide of ethyl, and when treated with an acid, loses its odour and is converted into a salt of ethylamine. (E. Meyer, *loc. cit.*)

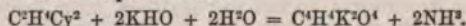
Cyanide of ethyl forms solid compounds with certain *metallic chlorides*, viz.  $\text{C}^2\text{H}^3\text{N}.\text{SbCl}^3$ ,  $\text{C}^2\text{H}^3\text{N}.\text{AsCl}^3$ ,  $\text{C}^2\text{H}^3\text{N}.\text{PtCl}^3$ ,  $2\text{C}^2\text{H}^3\text{N}.\text{SnCl}^4$ ,  $2\text{C}^2\text{H}^3\text{N}.\text{TiCl}^4$ ; and liquid compounds with *chloride of carbonyl*,  $\text{C}^2\text{H}^3\text{N}.\text{COCl}^2$ , and *chloride of cyanogen*,  $\text{C}^2\text{H}^3\text{N}.\text{CyCl}$ . (Henke, Ann. Ch. Pharm. cvi. 280.)

**CYANIDE OF ETHYLENE.**  $\text{C}^2\text{H}^2\text{N}^2 = (\text{C}^2\text{H}^4)^{\cdot}\text{Cy}^{\cdot}$ . (Maxwell Simpson, Proc. Roy. Soc. x. 574. Geuther, Ann. Ch. Pharm. cxx. 268.)—Produced by the action of cyanide of potassium on bromide or chloride of ethylene:



A mixture of 1 at. bromide of ethylene and 2 at. cyanide of potassium, with a considerable quantity of alcohol of specific gravity 0.840, is cohobated in the water-bath till the reaction is complete; the alcoholic liquid is then decanted and freed from alcohol by distillation; the semi-fluid residue is filtered at  $100^\circ\text{C}$ .; the filtrate is treated with a saturated solution of chloride of calcium; and the cyanide of ethylene, which rises to the surface in the form of a reddish oil, is washed with ether, and heated for some time to  $140^\circ\text{C}$ . to free it from admixed bromide of ethylene: this treatment does not, however, render it quite pure (Simpson). Geuther prepared the compound from chloride of ethylene, but the preparation is more difficult than with the bromide.

Cyanide of ethylene is, at ordinary temperatures, a brownish, semi-solid, crystalline mass, melting at  $50^\circ\text{C}$ . It dissolves readily in water and alcohol, less in ether. It cannot be distilled, but bears a tolerably high temperature without much decomposition. With nitric acid it forms a body which crystallises from alcohol in long needles. Heated with alcoholic potash, it acts similarly to cyanide of ethyl, giving off ammonia, and yielding succinate of potassium:



**CYANIDES OF GOLD.** Gold unites with cyanogen in two proportions, forming the aurous and auric cyanides; the latter, however, is known only in combination.

**PROTOCYANIDE OF GOLD OR AUROUS CYANIDE**,  $\text{AuCy}$ , is obtained by heating aurocyanide of potassium with nitric or hydrochloric acid. It is a lemon-yellow, crystalline powder, which, when examined by the microscope, appears to consist of hexagonal plates. It is insoluble in water, alcohol, and ether, has neither taste nor smell, and is not altered by exposure to the air. When heated, it gives off cyanogen and leaves metallic gold. It is not decomposed by nitric, hydrochloric, or sulphuric acid, even at the boiling heat; nitro-hydrochloric acid decomposes it slowly. Sulphuric acid has no action upon it; sulphhydrate of ammonium dissolves it to a colourless liquid, from which acids throw down sulphide of gold. It is soluble in ammonia. Potash decomposes it at the boiling heat, throwing down metallic gold. It is likewise soluble in hyposulphite of sodium.

Protocyanide of gold dissolves in the alkaline cyanides, forming double salts called aurocyanides, which precipitate the salts of other metals.

*Aurocyanide of Ammonium*,  $\text{NH}^4\text{AuCy}^2$ , or  $\text{NH}^4\text{Cy}.\text{AuCy}$ , is obtained by mixing the saturated solutions of sulphate of ammonium and aurocyanide of potassium, pre-

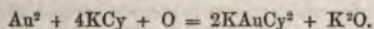


precipitating the sulphate of potassium and the excess of sulphate of ammonium with absolute alcohol, and leaving the filtrate to crystallise by evaporation. It forms colourless anhydrous crystals having a strong metallic taste.

The solution of protocyanide of gold in boiling aqueous ammonia yields, on cooling, grey, shining scales, which give up their ammonia when heated, or on addition of hydrochloric acid.

*Aurocyanide of Potassium*,  $\text{KAuCy}^2$ , may be obtained by dissolving aurous cyanide, auric oxide, or fulminating gold, in cyanide of potassium, the solution being attended with evolution of cyanogen in the second case, and of ammonia in the third. A convenient method of preparation is to dissolve 7 pts. of gold in nitro-muriatic acid, precipitate by excess of ammonia, and introduce the precipitate, after thorough washing, into a boiling solution of 6 parts of cyanide of potassium. The colourless solution, if not too dilute, deposits the aurocyanide in crystals on cooling. The mother-liquor yields by evaporation a fresh quantity of the salt, but very impure; it is evaporated with excess of hydrocyanic acid, and the residual aurous cyanide is washed with water and dissolved in cyanide of potassium (77 pts. cyanide of gold to 23 pts. of cyanide of potassium). The crystals are purified by recrystallisation from boiling water.

According to Prince Bagration (*J. pr. Chem.* xxxi. 367), metallic gold precipitated by ferrous sulphate dissolves in aqueous cyanide of potassium, slowly also in ferrocyanide of potassium, forming aurocyanide of potassium. The action requires, however, access of air, as shown by Elsner (*ibid.* xxxvii. 333), and is attended with formation of caustic potash:



Aurocyanide of potassium forms colourless elongated rhomboidal octahedrons or nacreous scales. It is permanent in the air, moderately soluble in water, sparingly in alcohol, insoluble in ether. Heated in a close vessel, it gives off cyanogen gas and leaves a mixture of gold and cyanide of potassium. Aqueous acids slowly decompose the solution, eliminating hydrocyanic acid, and precipitating aurous cyanide. Boiled with hydrochloric acid, it yields about 88 per cent. cyanide of potassium, together with chloride. A similar decomposition is produced by sulphuric, nitric, oxalic, and tartaric acids. Alkaline sulphhydrates do not decompose it. The aqueous solution mixed with mercuric chloride, yields, without evolution of hydrocyanic acid, a yellow precipitate, which increases on boiling, and assumes the deep yellow colour of aurous cyanide: the liquid contains cyanide of mercury and chloride of potassium, but no gold.

Aurocyanide of potassium is extensively used in electro-gilding. Its aqueous solution, especially when hot, gilds copper and silver, even without the aid of a voltaic battery, its place in the solution being supplied by an equivalent quantity of the other metal.

To obtain the gold which remains in the solution after it has been used for gilding, it should be evaporated to dryness, the residue finely pulverised and intimately mixed with an equal weight of litharge, then melted at a strong red heat, and the lead extracted from the button of lead and gold by warm nitric acid; the gold then remains in the form of a loose, yellowish-brown, spongy mass. (Böttger, *J. pr. Chem.* xxxvi. 169.)

The solution of aurocyanide of potassium forms a white precipitate with zinc-salts; yellowish-white with tin-salts; white with lead-salts; white with ferrous salts, changing to blue on addition of nitric acid; white with nitrate of silver; with chloride of manganese it forms small crystals.

**TRICYANIDE OF GOLD, OR AURIC CYANIDE.**  $\text{AuCy}^3$ .—This compound is obtained, in the free state, according to Himly, by decomposing auricyanide of potassium with any of the stronger acids. It is more probable, however, as pointed out by L. Gmelin (*Handbook*, viii. 37), that the substance thus separated is auricyanide of hydrogen,  $\text{HCy}.\text{AuCy}^2$ :



Moreover, as observed by Himly himself, the compound, when heated, gives off at first, not cyanogen, but hydrocyanic acid.

To prepare *auricyanide of hydrogen*, or *auriprussic acid*, an aqueous solution of auricyanide of potassium is mixed with excess of nitrate of silver; the liquid, containing the excess of the silver-salt, together with nitrate of potassium, is filtered; the precipitate, consisting of  $\text{AgCy}.\text{AuCy}^2$ , is thoroughly washed with water, then diffused in water, and decomposed with frequent agitation, and at the ordinary, or at a very slightly elevated temperature (at higher temperatures a yellow colouring will appear, and protocyanide of gold will be formed), by a quantity of hydrochloric acid, not sufficient to decompose the whole; and the filtrate is evaporated to dryness in

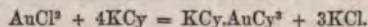


vacuo over oil of vitriol and lime.—Or, auricyanide of potassium is mixed with hydrofluosilicic acid and evaporated to dryness; the residue exhausted with absolute alcohol; and the solution filtered from the silico-fluoride of potassium, and left to evaporate (Himly). The product thus obtained generally has a yellowish colour, arising from the admixture of a small quantity of protocyanide; it must therefore be dissolved in the smallest possible quantity of water or alcohol, and the filtrate left to evaporate in the air or in vacuo; for the application of heat would reproduce protocyanide of gold. (Himly.)

Auricyanide of hydrogen forms large colourless laminæ and tables, containing 3 at. water of crystallisation =  $2\text{Au}^{\text{III}}\text{HCy}^{\text{I}} + 3\text{H}^{\text{O}}$  (Himly). They fuse at  $50^{\circ}\text{C}$ ., first giving off hydrocyanic acid, then cyanogen gas, and leave carbide of gold, which burns readily in the air, and is converted into pure gold. The aqueous solution, when evaporated over the water-bath, deposits part of the gold in the form of protocyanide. A boiling aqueous solution of *oxalic acid* exerts no reducing action. *Mercurous* or *mercuric nitrate*, heated with the solution, throws down protocyanide of gold, while cyanide of mercury remains in solution. *Mercuric chloride* forms no precipitate, even when the solution is heated. Auricyanide of hydrogen does not become moist when exposed to the air, but dissolves in water in every proportion, and almost as easily in alcohol and ether. (Himly.)

*Auricyanide of Ammonium*,  $(\text{NH}^{\text{I}})\text{Au}^{\text{III}}\text{Cy}^{\text{I}}$ .—Hydrated auric oxide is added to hydrocyanate of ammonia, obtained by distilling ferrocyanide of potassium with sal-ammoniac and water, as long as it continues to dissolve; the colourless filtrate is heated, which causes a large quantity of ammonia to escape; the filtrate evaporated over the water-bath, during which process it becomes covered with a rusty yellow film; the dry residue exhausted with water; and the filtrate left to evaporate till it crystallises. The salt forms large, colourless, four and six-sided tables, which give off 5.06 per cent. of water at  $100^{\circ}\text{C}$ ., and turn reddish-white, yellow at a higher temperature, and give off hydrocyanate of ammonia, and when ignited in the air leave 68.7 per cent. of pure gold. They dissolve readily in water and alcohol, but are nearly insoluble in ether. (Himly, *Ann. Ch. Pharm.* xlii. 343.)

*Auricyanide of Potassium*,  $\text{KAu}^{\text{III}}\text{Cy}^{\text{I}}$ .—Formed by converting 7 pts. of gold into a solution of the chloride as neutral as possible, and gradually adding this liquid to a hot concentrated aqueous solution of 8 pts. cyanide of potassium. The colourless mixture, as it cools, deposits crystals, which may be purified by recrystallisation:



(Himly, *Ann. Ch. Pharm.* xlii. 340.) A similar process is adopted by Rammelsberg (*Pogg.* *Ann.* xlii. 133). According to Glassford and Napier, on the other hand, this mode of preparation yields, not auricyanide, but aurocyanide of potassium.

The salt forms large, colourless tables, which, when exposed to the air, effloresce quickly and turn milk-white; in vacuo (Himly) or at  $100^{\circ}\text{C}$ . (Rammelsberg), they give off all their water of crystallisation. The residue then melts to a brown liquid, from which part of the gold separates out, an evolution of cyanogen taking place at the same time (Rammelsberg). The salt, when heated, gives off 2 at. cyanogen, and is converted into aurocyanide of potassium,  $\text{KC}y.\text{AuCy}$  (Himly).—Chlorine exerts a decomposing action only when aided by heat, chloride of cyanogen being then formed (Rammelsberg). Acids added to the solution of the salt produce no precipitate, but colour it yellow and eliminate hydrocyanic acid (Rammelsberg). *Mercurous nitrate*, boiled with the solution, forms a yellowish precipitate (Himly). The salt does not dissolve in absolute alcohol (Himly). Its aqueous solution is the best of all materials for galvanic gilding. (Meillet.)

*Auricyanide of Silver* is a curdy precipitate, formed by mixing the potassium-salt with nitrate of silver. It is soluble in ammonia, insoluble in nitric acid.

**CYANIDE OF HYDROGEN.** *Hydrocyanic* or *Cyanhydric acid*,  $\text{CNH}$  or  $(\text{C}^{\text{I}}\text{NH}) = \text{HCy}$ . *Prussic acid*, *Acidum borussicum*, *Blausäure*, *Berlinerblausäure*.—This acid was discovered by Scheele in 1782 (*Opuscula*, ii. 148), further examined by Berthollet (*Mém. de l'Acad. d. Sc. de Paris*, 1787, p. 148), Proust (*Ann. Chim.* ix. 185, 225) and Ittner (*Beiträge zur Geschichte der Blausäure*, 1809), and first obtained in the pure and liquid state by Gay-Lussac in 1811 (*Ann. Chim.* lxxvii. 128; xcv. 136). It appears, however, to have been known to the Egyptian priests, who used it for poisoning the initiated who had been guilty of divulging the sacred mysteries. (Hoefer, *Histoire de Chimie*, i. 226.)

*Occurrence*.—The kernels of bitter almonds, peaches, apricots, plums, cherries, and quinces,—the blossoms of the peach, sloe, and mountain-ash,—the leaves of the peach, cherry-laurel, and Portugal laurel,—the young branches of the peach,—the stem-bark of the Portugal laurel and mountain-ash, and the roots of the last-named tree, when

soaked in water and distilled after a while, yield hydrocyanic acid, together with bitter almond oil. The juice of the root of *Jatropha Manihot* also yields hydrocyanic acid when distilled. But it is only in the moister parts of these substances that the acid exists ready formed; the greater part is produced during immersion in water, the amygdalin contained in the plants being then resolved, by the fermentative action of the emulsin, also present, into glucose, bitter almond oil, and hydrocyanic acid (i. 202), the last two substances passing over in the distillation.

*Formation.*—1. From metallic cyanides, by the action of sulphydric, sulphuric or hydrochloric acid.—2. In the dry distillation of azotised bodies, and by the action of nitric acid on certain organic substances,—in the preparation of nitrous ether for example. It is also found among the products obtained by distilling albumin, fibrin, casein, or gelatin with sulphuric acid and chromate of potassium, or sulphuric acid and peroxide of manganese.—3. By the action of heat on formate of ammonium:  $\text{CH}(\text{NH}')\text{O}^2 = \text{CNH} + 2\text{H}^2\text{O}$  (Döbereiner, Buchner's *Repert.* xv. 425).—4. By the decomposition of amygdalin (i. 222).—5. By the decomposition of various cyanogen compounds and of fulminates.

*Preparation.*—1. *Of the aqueous acid.*—*a. From hydrated Ferrocyanide of potassium.*—This salt, which consists of  $\text{K}'\text{Fe}^2\text{Cy}^*.3\text{H}^2\text{O}$ , is decomposed when heated above  $100^\circ\text{C}$ . with sulphuric acid and water, in such a manner that half the cyanogen passes over in the form of hydrocyanic acid, whilst a yellowish-white powder,  $\text{K}'\text{Fe}^2\text{Cy}^*$ , is precipitated, and the residual liquid contains acid sulphate of potassium. The best proportion is 2 at. ferrocyanide of potassium to 6 at. sulphuric acid; therefore 2 . 211.4 pts. (= 422.8 pts.) ferrocyanide of potassium, to 6 . 49 (= 294 pts.) oil of vitriol (diluted with any convenient quantity of water),—therefore nearly 10 pts. of the ferrocyanide to 7 pts. oil of vitriol (Everitt, *Phil. Mag.* [3] vi. 97):



According to this calculation, 422.4 pts. ferrocyanide of potassium yield 3 . 27 (= 81) pts. hydrocyanic acid (in the anhydrous state), or 100 pts. ferrocyanide yield 19.16 pts. of the acid. Geiger obtained by experiment 17.07, and Wackenroder 17.26.—A larger quantity of sulphuric acid does not act further on the precipitated  $\text{K}'\text{Fe}^2\text{Cy}^*$ , and cannot therefore lead to a more abundant evolution of hydrocyanic acid; on the contrary, as it can no longer be taken up by the potash, it decomposes part of the liberated hydrocyanic acid into ammonia and formic acid, and consequently the hydrocyanic acid which distils over is smaller in quantity and contaminated with formic acid. It is better indeed to reduce the quantity of sulphuric acid to one-half (3.5 pts. oil of vitriol to 10 pts. ferrocyanide of potassium), so that neutral sulphate of potassium may be formed instead of acid sulphate; as, however, the neutral sulphate is but sparingly soluble, and is therefore deposited in the crystalline form during the distillation, it increases the percussive ebullition caused by the white crystalline powder, so that drops of the mixture are often thrown up, and mix with the distillate. Hence it is good to throw a few clippings of platinum-foil into the mixture.

The greater part of the hydrocyanic acid goes over in the beginning of the distillation at a temperature somewhat above  $100^\circ\text{C}$ .; and when the residual liquid attains a higher temperature, the water follows, containing but little hydrocyanic acid. A good condensing apparatus is therefore necessary; otherwise the hydrocyanic acid, which passes over at first,—since its boiling point is not above  $27^\circ\text{C}$ .,—will for the most part escape in vapour together with the air of the apparatus. Water in the receiver likewise tends to prevent this loss. It is not necessary to boil the residue down to dryness; it is sufficient indeed to distil off from  $\frac{3}{4}$  to  $\frac{2}{3}$  of the liquid, according to the quantity of water present.

It is unnecessary to dissolve the ferrocyanide in water before adding the sulphuric acid, as it readily dissolves in the water as the distillation goes on.

The distillatory apparatus must be so arranged as to prevent any portion of the mixture from spiriting over—to contain but little air, inasmuch as the air in escaping always carries hydrocyanic acid vapour with it—and to present the greatest possible amount of cooling surface.

If the distillate should become contaminated with sulphate of potassium and prussian blue by spiriting, it must be carefully rectified over a small quantity of magnesia, chalk, or carbonate of barium, in an apparatus affording ready means of condensation. This, however, occasions loss of prussic acid, and the rectified acid is much more prone to spontaneous decomposition.

*b. From Cyanide of Potassium.*—This salt is sometimes used for the preparation of hydrocyanic acid, because it is easily decomposed by dilute acids, even at ordinary temperatures. There is, however, greater difficulty in obtaining it in a pure and definite state, and, consequently of determining the exact amount of prussic acid that it will yield, a point of great importance in the preparation of the medicinal acid. Ordinary cyanide

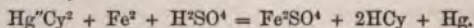


of potassium, prepared by Liebig's process (see CYANIDE OF POTASSIUM), is not well adapted for the purpose, because it contains a considerable quantity of cyanate and carbonate of potassium, and the carbonic acid evolved by the decomposition of these salts prevents, to a considerable extent, the condensation of the hydrocyanic acid; moreover, the cyanic acid which also passes over is soon resolved into carbonic acid and ammonia, and the latter induces spontaneous decomposition of the hydrocyanic acid. It is necessary, therefore, to use cyanide of potassium free from cyanate, which, according to Wöhler, may be prepared by fusing in a covered crucible a mixture of dehydrated ferrocyanide of potassium, burnt tartar, and charcoal powder (p. 217). The cooled mass is then lixiviated with cold water, and the filtered solution of cyanide of potassium is distilled with sulphuric acid.

By the following method an acid of nearly definite strength may be obtained without distillation.

To a solution of 9 pts. tartaric acid in 60 pts. water, contained in a well-stoppered bottle nearly filled with it, 4 pts. of pure cyanide of potassium are added; the vessel is shaken, frequently dipped into cold water, and then left in the cold for twelve hours; and the aqueous hydrocyanic acid, which contains but a very small quantity of tartrate of potassium, is poured off from the crystallised tartrate (Th. Clarke, Lond. Med. Surg. J. vi. 524; also J. Chim. méd. vii. 544). According to calculation, this acid contains 3.6 per cent. of anhydrous prussic acid.

c. *From Cyanide of Mercury*.—1. Cyanide of mercury is agitated with iron filings, sulphuric acid, and water in a well-stoppered bottle, till the liquid no longer tastes of mercury—or better, till a portion of it taken out is no longer blackened by sulphuretted hydrogen—the solution then decanted from the iron and mercury into a retort, and distilled (Scheele):



According to this equation, 126 pts. cyanide of mercury require 49 pts., or rather more, of oil of vitriol, together with a considerable quantity of water, and at least 28 pts. of iron filings; an excess of iron, however, accelerates the decomposition. If the cyanide of mercury be carefully weighed, this method is very well adapted to produce an acid of definite strength. The acid distils over at a gentle heat. (Gmelin.)

2. Sulphydric acid gas is passed through an aqueous solution of cyanide of mercury as long as it is absorbed, and the solution separated by filtration from the sulphide of mercury (Proust, Vauquelin):



Vauquelin, who employs a solution of 1 pt. cyanide of mercury in 8 pts. water, frees the solution from excess of sulphuretted hydrogen by agitation with carbonate of lead, till fresh portions of that salt are no longer browned by it, and filters the liquid again. But even if these filtrations be performed in a well-covered filter, a considerable quantity of prussic acid is lost by evaporation, so that this process never yields an acid of definite strength; moreover, the acid thus prepared is apt to be somewhat contaminated with sulphocyanic acid and oxide of lead.

d. *From Cyanide of Silver*.—200 pts. of pure cyanide of silver are shaken up with 240 pts. hydrochloric acid of specific gravity 1.129, and, when the decomposition is complete, the hydrocyanic acid is separated from the chloride of silver by decantation (Everitt, Phil. Mag. [3] vi. 100).—This hydrocyanic acid may contain a small quantity of hydrochloric acid, but has the advantage of definite strength.

e. *From Cyanide of Lead*.—Pure cyanide of lead is decomposed by an equivalent quantity of dilute sulphuric acid (Thomson). As, however, the cyanide of lead is difficult to dry, the quantity of sulphuric acid required cannot be exactly determined; if too little be used, lead remains in solution. (Souberain, N. J. Pharm. i. 121.)

f. Hydrocyanic acid of perfectly definite strength can only be obtained by mixing weighed quantities of the anhydrous acid and water. Acid of the so-called Scheele's strength contains 5 per cent. of the anhydrous acid.

II. *Preparation of Anhydrous Hydrocyanic Acid*.—The great volatility and highly poisonous character of hydrocyanic acid renders this process very dangerous; it should therefore only be performed in winter, and with the aid of a freezing mixture.

It may be prepared directly by slowly passing dry sulphydric acid gas through a tube filled with dry cyanide of mercury—except at the further end, where there is placed a small quantity of carbonate of lead—and connected with a U-tube surrounded with ice and salt. The anhydrous acid then passes over and collects in the receiver in the liquid form. The passage of the gas must be stopped as soon as the carbonate of lead begins to blacken. (Vauquelin.)

A better mode of preparation, however, is to dehydrate the strong aqueous acid, obtained by either of the preceding processes, with fused and pulverised chloride of



calcium. Trautwein (Repert. xi. 13) distils 15 pts. of ferrocyanide of potassium with 9 pts. oil of vitriol and 9 pts. water, till 4 or 5 pts. of strong acid have passed over into the receiver, which must be surrounded with ice, or with a mixture of ice and salt; pours the acid into a strong bottle provided with a good stopper and kept cold by a freezing mixture; and adds pulverised chloride of calcium in small successive portions, and with frequent agitation, so that no great development of heat may take place. The mixture, after being left at rest for a while, separates into two layers, the lower one consisting of aqueous chloride of calcium, and the upper of hydrocyanic acid freed from part of the water. The acid is then poured into another bottle, and again treated with chloride of calcium; and this treatment is continued till fresh quantities of chloride of calcium added to the acid no longer become pasty and cake together, but remain pulverulent. By this treatment, Trautwein obtains from 2 to 2½ pts. of anhydrous acid. Since a considerable quantity of acid is lost at each decantation, and moreover the vapour which escapes may exert a poisonous action, it is better to leave the acid in the first bottle and draw off the solution of chloride of calcium by a siphon. This siphon is filled with a saturated solution of chloride of calcium, closed with the finger at the end of the longer arm, and not opened till the shorter arm is depressed to the lowest part of the bottle held in a somewhat inclined position. As soon as the chloride of calcium solution has completely run out, the siphon is again closed with the finger and taken out. More chloride of calcium is then introduced, &c. As soon as a fresh portion of that substance no longer becomes pasty, the acid may be decanted into a well-cooled bottle containing pulverised chloride of calcium, and finally into a clean bottle (Gmelin). Or the acid, after being left for some time in contact with chloride of calcium, may be distilled off at the heat of the water-bath, the bottle being connected by a bent tube with a U-tube immersed in ice and salt.

Another method is to pass the vapour of the aqueous acid directly over chloride of calcium, which abstracts the water. A mixture of 8 pts. ferrocyanide of potassium, 3 pts. burnt tartar, and 1 pt. charcoal is fused in a covered crucible; the fused mass digested with six times its weight of water in a vessel which can be closed; and the clear solution decanted from the sediment of iron and charcoal into a tubulated retort, which is connected with a glass tube horizontal in the nearer part, bent downwards at a certain distance from the retort, and passing into a U-tube. This U-tube is placed within a cylinder containing cold water, and is filled with chloride of calcium, excepting at the end where the vapours enter, and at this end are placed small pieces of the fused mixture above mentioned. The other end of the U-tube is connected by a bent tube with the glass which serves as a receiver, and is surrounded with ice, or better, with a freezing mixture. A cooled mixture of 1 pt. oil of vitriol (the fused mixture whose solution is contained in the retort being supposed = 2) and 1 pt. water, is then poured into the retort by small portions at a time through a funnel-tube adapted to the tubulus. The mixture starts spontaneously into strong ebullition, so that the sulphuric acid must be added slowly; and the greater part of the hydrocyanic acid distils over without the application of heat. Finally, when all the sulphuric acid has been added, and the boiling has ceased, the retort is heated till the contents begin to boil gently; and the cylinder in which the chloride of calcium tube is immersed is emptied of cold water, and filled with water at 30°–35°, to volatilise the prussic acid there condensed, and cause it to pass over into the receiver (Wöhler, *Berzelius Lehrs.* i. 816). As the U-tube sometimes becomes stopped up, Wöhler further recommends that the neck of the retort be inclined upwards at an angle of about 45°, and an intermediate vessel, containing a small quantity of chloride of calcium or cyanide of potassium, placed between the retort and the U-tube. The chloride of calcium tube and the intervening vessel are immersed, from the beginning of the operation, in water at 30° C., and the prussic acid vapour is condensed in a tall narrow vessel, surrounded with a mixture of ice and salt; the acid is then obtained in the form of a crystalline mass.

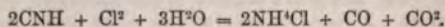
*Properties.*—Anhydrous hydrocyanic acid is, at common temperatures, a colourless liquid, of sp. gr. 0.7058 at 7° C., and 0.6969 at 18° C. (Gay-Lussac); it solidifies at 15° C., in feathery crystals. It boils at 26.5° C. Vapour-density, 0.947 by experiment (Gay-Lussac), by calculation,  $\frac{26 + 1}{2} = 13.5$ , referred to hydrogen as unity, =  $13.5 \times 0.0693 = 0.9405$  referred to air. It dissolves in water in all proportions, forming a solution which is lighter than water, and reddens litmus slightly; it is also miscible with alcohol.

The anhydrous acid or the strong aqueous solution burns with a faint violet flame. It has a peculiar odour like that of bitter almonds. It is excessively poisonous; a drop of the anhydrous acid producing instant death when swallowed. The vapour of the anhydrous or of the highly concentrated aqueous acid, is likewise instantly fatal when inhaled; the vapour diluted with air produces, when inhaled in small quantity, a peculiar irritation in the throat; in larger quantity, giddiness and head-ache. The

dilute aqueous acid has a cooling taste, with pungent bitter aftertaste; it is much used in medicine to allay irritation.

*Decompositions.*—1. The anhydrous acid quickly undergoes spontaneous decomposition, giving off ammonia and leaving a brown substance. The aqueous acid undergoes the same decomposition, part of it being, however, converted into formate of ammonium:  $\text{CNH} + 2\text{H}^2\text{O} = \text{CH}(\text{NH}^4)\text{O}^2$ . The decomposition takes place more quickly as the acid is stronger; the addition of a small quantity of another acid renders it more permanent; alkalis, on the other hand, accelerate the decomposition. Exposure to light also causes the change to take place more quickly; hence the acid should always be kept in the dark, or in bottles covered with black paper.—2. The vapour of hydrocyanic acid passed through a *red-hot tube*, is partly resolved into cyanogen and hydrogen gases; at the same time, however, a small quantity of nitrogen is set free and charcoal separated.—3. By *electricity*. The vapour of hydrocyanic acid is but slowly decomposed by the electric spark, with separation of a small quantity of carbon. The aqueous acid is decomposed by the voltaic current, hydrogen being evolved at the negative pole, while the cyanogen set free at the positive pole either remains dissolved or unites with the metal which forms the pole.—4. By *oxidation*. The anhydrous acid and its vapour, when set on fire, burn in contact with air or oxygen gas, producing carbonic anhydride, nitrogen, and water. The vapour mixed with oxygen explodes with great violence on the passage of an electric spark. For complete combustion, 2 volumes of the vapour require  $2\frac{1}{2}$  vols. oxygen, and after the explosion, there remain 3 vols. of gas consisting of 2 vols. carbonic anhydride and 1 vol. nitrogen. Hence the composition of the vapour is determined: for the 2 vols. carbonic anhydride contain 2 vols. oxygen; consequently, the remaining  $\frac{1}{2}$  vol. oxygen has been consumed in combining with the hydrogen (1 vol.) to form water. Hence the 2 vols. hydrocyanic vapour contain 1 at. carbon, 1 at. nitrogen, and 1 at. hydrogen. Many *metallic oxides* decompose hydrocyanic acid even at common temperatures; peroxide of lead forms with it, according to Liebig, cyanide of lead, water, and cyanogen.—The vapour of the acid mixed with hydrogen gas is completely absorbed by peroxide of manganese, without separation of cyanogen (Gay-Lussac). Basic metallic oxides generally convert the acid into water and a metallic cyanide.—5. By *chlorine*. The anhydrous acid poured into a bottle filled with dry chlorine, and exposed to sunshine, forms hydrochloric acid and solid chloride of cyanogen.

In presence of aqueous vapour, but little chloride of cyanogen is formed, the chief products of the reaction being sal-ammoniac, carbonic oxide, and carbonic anhydride:



Chlorine gas passed into dilute hydrocyanic acid forms hydrocyanate of chloride of cyanogen,  $\text{C}^2\text{N}^2\text{Cl}^2.\text{CNH}$  (Wurtz, Ann. Ch. Pharm. lxxix. 280). When chlorine gas is passed into a mixture of strong aqueous hydrocyanic acid and alcohol, till carbonic acid begins to escape, a crystalline compound,  $\text{C}^2\text{H}^2\text{NClO}^2$ , is formed, sparingly soluble in cold water and in ammonia, somewhat more in boiling water, easily in alcohol and in ether. The same compound is formed on passing chlorine into an alcoholic solution of cyanide of mercury (*q. v.*) (Stenhouse.)

6. Bromine decomposes the aqueous acid, forming bromide of cyanogen. 7. *Iodine* does not decompose the vapour of hydrocyanic acid (Gay-Lussac). With the aqueous acid it forms hydriodic acid and liberates cyanogen. (Porrett.)

8. By *acids*. Strong hydrochloric or moderately dilute sulphuric acid decomposes hydrocyanic acid in a few minutes, even in the cold, and more quickly with aid of heat, into formic acid and ammonia,  $\text{CNH} + 2\text{H}^2\text{O} = \text{CH}^2\text{O}^2 + \text{NH}^3$ . Hydrochloric acid acts more quickly than sulphuric acid; the latter, if too strongly heated, further resolves the formic acid into water and carbonic oxide (Pelouze, Ann. Ch. Pharm. ii. 84). Small quantities of either of these acids, however, retard the spontaneous decomposition of prussic acid. (Gm. vii. 403.)

9. The *fixed alkalis*, at high temperatures, likewise resolve hydrocyanic acid into ammonia and formic acid.

10. *Potassium* burns when heated in the vapour of hydrocyanic acid, with formation of cyanide of potassium and evolution of hydrogen.

*Detection and Estimation of Hydrocyanic acid.*—1. Free hydrocyanic acid, if not too dilute or mixed with other odoriferous substances, may be recognised by its characteristic odour (p. 217).—2. On making the solution alkaline with *potash*, adding a solution of *ferrous sulphate* oxidised by exposure to the air, and then sufficient hydrochloric acid to dissolve the precipitated ferroso-ferrie oxide, prussian blue remains undissolved if hydrocyanic acid was present; otherwise a clear yellow-green solution is formed. If the quantity of hydrocyanic acid present is very small, the liquid appears clear at first, but after standing for some time, deposits dark blue flocks.—3. The liquid to



be tested is mixed with a few drops of yellow sulphide (persulphide) of ammonium and evaporated to dryness over the water-bath, to convert the hydrocyanic acid into sulphocyanate of ammonium. On dissolving the residue in water and testing with sesquichloride of iron, the liquid assumes the deep blood-red colour of ferric sulphocyanate. This test, according to Taylor (Ann. Ch. Pharm. lxx. 263), is capable of distinctly showing the presence of  $\frac{1}{3930}$  of a grain of anhydrous prussic acid in a very

dilute liquid, whereas the prussian blue test will not detect less than  $\frac{1}{780}$  of a grain.

—4. Hydrocyanic acid gives, with *nitrate of silver*, a white precipitate of cyanide of silver, which dissolves in ammonia as easily as the chloride, but is distinguished therefrom by not blackening when exposed to light, and by dissolving in strong nitric acid at the boiling heat with evolution of carbonic acid. The precipitated cyanide shaken up with dilute hydrochloric acid, emits the characteristic odour of prussic acid.

—5. On rendering the liquid alkaline with potash, then adding *sulphate of copper*, and just sufficient hydrochloric acid to dissolve the blue precipitate of cupric hydrate, white cuprous cyanide remains undissolved if the liquid contained prussic acid (Lassaigne). This reaction is, however, less characteristic than those before mentioned, inasmuch as a similar effect is produced by hydriodic acid.

When liquids containing blood, articles of food, or parts of the animal body, are to be examined for prussic acid, as in cases of poisoning, advantage is taken of the extreme volatility of the acid, to separate it from the substances which might disguise its reactions. A good method of testing is to place a portion of the suspected matter on a watch-glass, cover it with another watch-glass, on the concave surface of which is placed a drop of yellow sulphide of ammonium, leave it for ten minutes, then evaporate the sulphide of ammonium to dryness at a gentle heat, and moisten the residue with a drop of solution of ferric chloride, which, if prussic acid was present, will produce the blood-red colour above mentioned. If larger quantities of material have to be operated on, it is best to distil off the acid at the heat of the water-bath, acidulating with tartaric acid if the original liquid is alkaline. The distillate may then be tested by any of the methods above given.

*Quantitative Estimation.*—The strength of aqueous prussic acid cannot be determined by its specific gravity, the variation from 1.6 to 16 per cent. being only from 0.9979 to 0.9570. The percentage of real acid is therefore determined by one of the following methods:

1. By *Mercuric oxide*. To a weighed quantity of the aqueous acid, a weighed quantity of finely pulverised red oxide of mercury is added, by small portions and with agitation, till the last portions added remain undissolved, and the odour of hydrocyanic acid is no longer perceptible. The weight of the remaining quantity of mercuric oxide deducted from the original weight, gives the weight of the quantity dissolved; and since 108 pts. of mercuric oxide require for solution 27 pts. of anhydrous prussic acid, it follows that 4 pts. of mercuric oxide dissolved indicate the presence of 1 pt. of anhydrous acid in the liquid under examination (Ure, Quart. J. of Sc. xiii. 321; also Schw. J. xxxvi. 282). As the cyanide of mercury thus formed is capable of taking up more of the mercuric oxide, even at ordinary temperatures, forming indeed, the compound  $\text{Hg}^{\circ}\text{O}.\text{Hg}^{\circ}\text{Cy}^2$ , this method is apt to give too great an amount of hydrocyanic acid, especially if the liquid be not kept cool, and the addition of mercuric oxide stopped as soon as the odour of hydrocyanic acid has disappeared. Moreover, it must first be ascertained that the prussic acid to be examined is free from hydrochloric acid, which would likewise dissolve mercuric oxide. In this case, Geoghegan saturates the hydrochloric acid with carbonate of calcium before adding the mercuric oxide.—This method is not applicable to cherry-laurel water, bitter almond water, &c., because these waters contain a vegetable acid, probably benzoic acid, which likewise dissolves mercuric oxide. (Duflos, Kastn. Arch. xiv. 88.)

2. *Nitrate of silver*, mixed with a small quantity of ammonia, such that the liquid after precipitation may be rather acid than alkaline, is dropped into the hydrocyanic acid, as long as any precipitate of cyanide of silver is produced; the precipitate is collected on a small filter, previously dried at  $100^{\circ}\text{C}$ . and weighed; and the precipitate and filter are washed and dried together at  $100^{\circ}$  and weighed. 134 pts. of cyanide of silver indicate 27 pts. of anhydrous prussic acid. The acid may also be precipitated by a mixture of nitrate of silver and ammonia, and nitric acid then cautiously added to the liquid till a slight acid reaction is produced (Duflos). This method is the most accurate of all.

If the liquid contains metallic chlorides, it is acidulated and treated with excess of nitrate of silver; and the mixed precipitate of cyanide and chloride of silver is dried and weighed as above, then treated with dilute hydrochloric acid, which converts it wholly



into chloride of silver, and weighed again. By the conversion of the cyanide of silver into chloride, the weight increases by 9.5 pts.  $[35.5 (\text{Cl.}) - 26 (\text{Cy.})]$ , so that every 9.5 pts. increase in the weight corresponds to 27 pts. anhydrous prussic acid.

The same method is applicable to the determination of hydrocyanic acid in presence of hydrobromic or hydriodic acid. From acids not precipitated by nitrate of silver from acid solutions, such as sulphuric and phosphoric acid, hydrocyanic acid is easily separated by this reagent.

3. *Volumetric method.*—1 at. cyanide of potassium forms with 1 at. cyanide of silver a soluble double cyanide, which is not decomposed by excess of alkali. If, then, a liquid containing hydrocyanic acid be mixed with solution of caustic potash till a strong alkaline reaction is produced, and then with a standard solution of nitrate of silver till the liquid begins to show turbidity, 1 at. of silver used will correspond exactly to 2 at. hydrocyanic present in the liquid. If the silver-solution be prepared by dissolving 3.150 grm. fused nitrate of silver in water, and diluting the solution to 1000 cub. cent., each cub. cent. of it used will correspond to 1 milligramme of anhydrous prussic acid. The presence of formic or hydrochloric acid has no influence on the result. This method is quite as accurate as the last, and is applicable to bitter almond water and laurel water, as well as to medicinal prussic acid. Bitter almond water, which is turbid from the presence of oily drops, must first be mixed with three or four times its bulk of water, to render it clear; otherwise the limit of the reaction will not be seen. (Liebig, *Ann. Ch. Pharm.* lxxvii. 102; *Chem. Soc. Qu. J.* iv. 219.)

#### *Compounds of Hydrocyanic acid with Metallic Chlorides.*

*Hydrocyanate of Antimonic Chloride,  $\text{SbCl}_3 \cdot 3\text{HCy.}$* —When the vapour of anhydrous prussic acid is brought in contact with pentachloride of antimony heated to  $30^\circ \text{C.}$ , this compound is produced in the form of clear definite prisms, which volatilise between  $70^\circ$  and  $100^\circ \text{C.}$ , but at the same time undergo partial decomposition, even in an atmosphere of carbonic acid. The compound is deliquescent; does not fume in the air; is decomposed by water, with separation of antimonic acid; and unites with ammonia, forming a brown-red pulverulent mass. (Klein, *Ann. Ch. Pharm.* lxxiv. 86.)

*Hydrocyanate of Ferric Chloride,  $\text{FeCl}_3 \cdot 2\text{HCy.}$* —Sublimed ferric chloride and anhydrous prussic acid unite, with a hissing noise, and form a brown-red liquid, which soon solidifies in the crystalline state. The compound deliquesces in the air, giving off hydrocyanic acid; melts at  $100^\circ \text{C.}$ ; and unites with ammonia, forming a greenish black powder, which dissolves in water, with separation of prussian blue and therefore contains protochloride of iron. The compound, when heated, yields ferruginous sal-ammoniac, hydrocyanic acid, and protochloride of iron. (Klein, *loc. cit.*)

*Hydrocyanate of Stannic Chloride,  $\text{SnCl}_4 \cdot 2\text{HCy.}$* —Tetrachloride of tin unites with anhydrous prussic acid, without sensible rise of temperature, forming a solid crystalline body; if the acid in the gaseous state be passed through a tube in which the stannic chloride is placed, so as to expose a large surface, the compound will be obtained in fine crystals. The crystals are colourless, refract light strongly, and appear to be isomorphous with the corresponding titanium-compound. In a stream of dry air they volatilise as quickly as anhydrous prussic acid, becoming at the same time white and opaque. They are decomposed by water and by damp air. They unite with ammoniacal gas, forming a white substance which may be sublimed. No analysis was made of this compound, on account of its great volatility; but it appears to be analogous to the titanium-compound. (Klein, *loc. cit.*)

*Hydrocyanate of Titanic Chloride,  $\text{TiCl}_4 \cdot \text{HCy.}$* —When anhydrous prussic acid is poured into tetrachloride of titanium, combination takes place, attended with rise of temperature and ebullition (on which account the substances must be cooled to  $0^\circ \text{C.}$  before mixing, or the hydrocyanic acid must be passed in the form of gas into the titanic chloride), and formation of a yellow pulverulent mass; the excess of prussic acid is then distilled off, and the compound sublimed by careful heating. It is very volatile, subliming below  $100^\circ \text{C.}$ , in the form of clear, shining, lemon-yellow crystals (rhombic pyramids and combinations thereof), which, if rapidly sublimed, unite into a coherent mass. It fumes slightly in the air; smells strongly of hydrocyanic acid; quickly turns white, and deliquesces to a clear viscid solution. Water dissolves it, with rise of temperature, and forms a clear solution; if the quantity of water be small, gaseous hydrocyanic acid is given off as the substance dissolves. It is not altered by sublimation in chlorine gas. When its vapour is passed through a red-hot glass tube, it covers the tube with copper-coloured nitride of titanium mixed with charcoal. (Wohler, *Ann. Ch. Pharm.* lxxiii. 226.)

**CYANIDES OF IRIDIUM.** The only known compound of iridium and cyanogen is the sesquicyanide, which forms with basic cyanides a group of salts, the

iridiocyanides,  $3\text{MCy}.\text{Ir}^2\text{Cy}^3 = \text{M}^3\text{Ir}^2\text{Cy}^6$ , analogous to the ferricyanides. They have been chiefly studied by C. A. Martius. (Ann. Ch. Pharm. cxvii. 357.)

*Iridiocyanide of Barium*,  $\text{Ba}^2\text{Ir}^2\text{Cy}^6 + 9\text{aq.}$ —To prepare this salt, platinum-ferrous iridiocyanide of copper, obtained in the treatment of platinum-residues by Martius' method\*, is digested with baryta-water, the excess of baryta removed by carbonic acid, and the filtrate left to crystallise: it then first deposits crystals of platinumocyanide, and afterwards of iridiocyanide of barium. The latter forms hard transparent crystals belonging to the trimetric system, and efflorescing in the air to a white powder still retaining 3 at. water. The salt dissolves easily in water, is insoluble in alcohol, and scarcely decomposable by acids. The aqueous solution forms with cupric salts a light blue precipitate, with mercurous, ferrous, lead, and zinc salts, white, and with ferric salts a yellow precipitate.

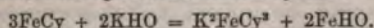
*Iridiocyanide of Hydrogen*,  $\text{H}^3\text{Ir}^2\text{Cy}^6$ .—Obtained by decomposing the barium salt with sulphuric acid, exhausting with ether, and evaporating. It forms small white crystalline crusts, has a strong acid reaction, decomposes carbonates, dissolves easily in water and in alcohol, with difficulty in ether, and has a nauseous metallic taste. Above  $300^\circ\text{C}$ . it assumes a colour varying from yellow to dark green, and gives off prussic acid. The aqueous solution mixed with hydrochloric acid deposits after a while, green sesquicyanide of iridium. (Martius.)

*Iridiocyanide of Potassium*,  $\text{K}^3\text{Ir}^2\text{Cy}^6$ .—Prepared: 1. By gently igniting a mixture of ferrocyanide of potassium and metallic iridium in a glass flask, exhausting the mass with hot water; filtering and evaporating, the liquid then depositing, first, crystals of ferrocyanide of potassium, and afterwards of the iridiocyanide (Wöhler and Booth, Pogg. Ann. xxxi. 167).—2. By melting chloriridate of ammonium with  $1\frac{1}{2}$  pts. pulverised cyanide of potassium in a porcelain crucible for 10 or 15 minutes, dissolving the mass in boiling water, and leaving the liquid to crystallise by cooling (Claus, Jahresber. d. Chem. 1855, p. 445).—3. By decomposing the copper-salt with potash-ley, or the barium-salt with sulphate of potassium (Martius). The salt is anhydrous, insoluble in alcohol, easily soluble in water, and separates from the aqueous solution in large, transparent, colourless, prismatic twin-crystals belonging to the trimetric system. It is not decomposed, even by ignition in a current of chlorine or hydrochloric acid. (Martius.)

Rammelsberg's analysis of this salt agrees best with the formula  $\text{K}^3\text{Ir}^2\text{Cy}^6$ , or  $2\text{KCy}.\text{Ir}^2\text{Cy}^3$ ; but those of Claus and of Martius lead to the formula  $\text{K}^3\text{Ir}^2\text{Cy}^6$ , corresponding with those of the other iridiocyanides.

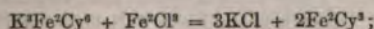
**CYANIDES OF IRON.** (Scheele, *Opuscula*, ii. 148.—Ittner, *Beiträge zur Geschichte der Blausäure*, Freib. Const. 1809.—Proust, Ann. Chim. ix. 185 and 225.—Vauquelin, *ibid.* v. 113.—Berzelius, Ann. Ch. Phys. [2] xv. 144 and 225; Pogg. Ann. xv. 385.—Porrett, Phil. Trans. 1814, p. 527; Ann. Phil. xii. 214; xiv. 295.—Robiquet, Ann. Ch. Phys. [2] xii. 275; xvii. 196; xlv. 279.—Thomson, Ann. Phil. xii. 202; xv. 392; xvi. 217.—Gay-Lussac, *ibid.* xlv. 73.—L. Gmelin, Schw. J. xxxiv. 325.—Pelouze, Ann. Ch. Phys. [2] lxxix. 40.—Rammelsberg, Pogg. Ann. xxxviii. 364; xlii. 3.—Bunsen, *ibid.* xxxiv. 131; xxxvi. 464.—Williamson, Ann. Ch. Pharm. lvii. 225.—Gm. vii. 429.—Gerh. i. 320.)

The protoxide and sesquicyanide of iron have not been obtained in very definite form. On adding cyanide of potassium to a ferrous salt, a yellowish-red flocculent precipitate is formed, consisting essentially of ferrous cyanide,  $\text{FeCy}$ , but always containing a certain quantity of cyanide of potassium, smaller, however, the more the iron-salt is in excess. This precipitate dissolves in excess of cyanide of potassium, and is converted into ferrocyanide of potassium; dilute potash-ley also converts it into ferrocyanide, with separation of ferrous hydrate:



When exposed to the air, it takes up oxygen and turns blue. (Fresenius, Ann. Ch. Pharm. cvi. 210.)

Sesquicyanide of Iron, or Ferric Cyanide,  $\text{Fe}^2\text{Cy}^3$ , is not known in the solid form. Ferricyanide of potassium forms with sesquichloride of iron a dark brown liquid, which may be regarded as a mixture of chloride of potassium and sesquicyanide of iron:



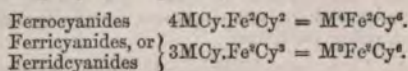
\* Chloriridate of ammonium (containing platinum and ruthenium) is fused with  $1\frac{1}{2}$  pt. cyanide of potassium, the cooled mass dissolved in a very small quantity of water, and the yellow filtrate (after all the free cyanide of potassium has been decomposed by dilute hydrochloric acid), is precipitated by sulphate of copper, whereby a precipitate is formed consisting mainly of platinumocyanide and iridiocyanide of copper. (See IRIDIUM and PLATINUM-METALS.)



but this solution decomposes on evaporation, becoming covered with a film of prussian blue, and giving off cyanogen or chlorine gas, according as the cyanide or the chloride is in excess. Neither is ferric cyanide obtained by adding cyanide of potassium to ferric chloride, the products formed being chloride of potassium, free hydrocyanic acid, and a precipitate of ferric hydrate.

Some of the compounds called prussian blues have the composition of cyanides of iron, intermediate between the proto- and sesquicyanide; but, from their mode of formation, they appear rather to be double cyanides.

The protocyanide and sesquicyanide of iron unite with other metallic cyanides, forming two very important groups of compounds, viz.:

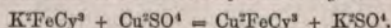


It will be seen from these formulæ that the ferro- and ferri-cyanides differ from one another only by one atom of metal; and, accordingly, it is found that the former are easily converted into the latter by the action of oxidising (metal-abstracting) agents, and the latter into the former, by the action of reducing (metal-adding) agents. Thus ferrocyanide of potassium,  $\text{K}^{\text{f}}\text{Fe}^{\text{c}}\text{Cy}^{\text{a}}$ , is easily converted into the ferricyanide,  $\text{K}^{\text{f}}\text{Fe}^{\text{f}}\text{Cy}^{\text{a}}$ , by the action of chlorine, and many double ferrocyanides may be formed from ferricyanides by the action of alkalis in presence of a reducing agent, e.g.  $\left. \begin{array}{c} \text{NH}^{\text{f}} \\ \text{K}^{\text{f}} \end{array} \right\} \text{Fe}^{\text{c}}\text{Cy}^{\text{a}}$ , from  $\text{K}^{\text{f}}\text{Fe}^{\text{f}}\text{Cy}^{\text{a}}$ , by the action of ammonia in presence of grape-sugar. For the several views entertained respecting the composition of these double cyanides, see page 201.

### Ferrocyanides, $\text{M}^{\text{f}}\text{Fe}^{\text{c}}\text{Cy}^{\text{a}}$ .

*Ferroproussiates, Hydroferrocyanates.*—The general formulæ of these compounds might evidently be halved, and, in fact, it is often more convenient to represent them by the simpler formula,  $\text{M}^{\text{f}}\text{Fe}^{\text{c}}\text{Cy}^{\text{a}}$ ; but the tetrabasic formula is justified by the existence of double ferrocyanides containing three atoms of one metal and one of another, such as  $(\text{NH}^{\text{f}})\text{K}^{\text{f}}\text{Fe}^{\text{c}}\text{Cy}^{\text{a}}$ ; and, as already observed, it has the advantage of showing clearly the relation between the ferro- and ferricyanides.

The ferrocyanides of the alkali-metals are obtained by neutralising ferroproussic acid with caustic alkalis or alkaline carbonates; by dissolving protocyanide of iron in aqueous solutions of alkaline cyanides, or in a mixture of alkaline carbonate and hydrocyanic acid; by treating protocyanide of iron, or a mixture of that compound with the sesquicyanide (prussian blue), with an aqueous alkali, whereby protoxide or sesquioxide of iron is formed; or by treating protoxide of iron with the aqueous solution of the cyanide of an alkali-metal, in which it dissolves with formation of alkali. The insoluble ferrocyanides are obtained by precipitating a soluble ferrocyanide with the solution of the salt of an earth-metal or a heavy metal: e.g. the copper-compound:

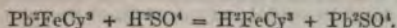


The ferrocyanides of the alkali-metals are colourless in the anhydrous, but yellow in the hydrated state; they exert no action on vegetable colours, have a faintly saline and bitter taste, and do not exhibit the violent action of hydrocyanic acid on the animal economy. The ferrocyanides of the earth-metals are white, and among those of the heavy metals, some are white, while others are distinguished by bright colours. Hence the use of alkaline ferrocyanides to discover the presence of titanium, tantalum, molybdenum, uranium, cobalt, nickel, and copper; but antimony, tellurium, platinum, rhodium, and iridium are not precipitated by alkaline ferrocyanides.

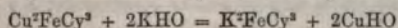
Those ferrocyanides which are deprived of all their water by a gentle heat, are decomposed at a higher temperature in the following manner: the cyanide of iron is always converted into carbide of iron, with evolution of nitrogen gas; but the other cyanide which is associated with it, either remains undecomposed, which is the case with cyanide of potassium, or is resolved into nitrogen and a metallic carbide, as with cyanide of lead; or into cyanogen gas and metal, as with cyanide of silver. If, however, the ferrocyanides are not completely dehydrated before being subjected to destructive distillation, they give off hydrocyanic acid, carbonic acid, and ammonia, and leave the two metals combined or mixed with a greater or smaller quantity of carbon. In the circuit of the voltaic battery, the aqueous solutions of the alkaline ferrocyanides yield alkali at the negative pole, and hydrocyanic acid and prussian blue at the positive pole, unless the positive polar wire is of copper, in which case the deposit there formed consists of cyanide of copper (Porrett). When ferrocyanides are heated with oil of vitriol to a temperature much above  $100^{\circ}\text{C}$ ., they give off, with strong



effervescence, sulphurous and carbonic anhydrides, and nitrogen, leaving a compound of sulphuric acid with ammonia, oxide of iron, and the oxide of the other metal (Berzelius). Besides the gases just mentioned, a large quantity of carbonic oxide is evolved, and a small quantity of sulphate of ammonium volatilises (Bunsen, Pogg. Ann. xxxiv. 132). See FERROCYANIDE OF POTASSIUM. The stronger acids withdraw the other metal from ferrocyanides, and thereby separate ferroproussic acid:



A similar effect is produced by sulphydric acid, if the other metal be precipitable from its solutions by that reagent. Many ferrocyanides of heavy metals are decomposed by aqueous alkalis, yielding an alkaline ferrocyanide and a hydrate of the heavy metal:



Neither alkalis nor sulphydric acid decompose the cyanide of iron contained in ferrocyanides.

Most ferrocyanides unite in their entire state with strong sulphuric acid, forming a kind of salt, in which they constitute the base. Their powder soaked in cold oil of vitriol swells up to a pasty compound, with loss of colour, and considerable evolution of heat, and, according to the nature of the metal present, either dissolves completely in a large excess of the acid, or remains almost undissolved, forming a solid compound with it. These compounds remain undecomposed even at temperatures much above  $100^{\circ}\text{C}$ . If a small quantity of water be added to the resulting solutions, e.g. by exposing them to the air, they frequently deposit a crystalline compound, which contains less sulphuric acid, and when treated with a larger quantity of water, is resolved either into ferroproussic acid and a compound of sulphuric acid with the other metallic oxide, or into metallic ferrocyanide and dilute sulphuric acid. (Berzelius, Schw. J. xxx. 35.)

**FERROCYANIDE OF ALUMINIUM**, obtained by saturating ferrocyanide of hydrogen (ferroproussic acid) with alumina, is uncrystallisable, and decomposes by evaporation.

Ferrocyanide of potassium added to an aluminium-salt, even if strongly acidulated, throws down the whole of the aluminium in the form of a white precipitate, which yields by analysis 14.87 per cent. aluminium, and 22.36 iron, and may therefore be represented by the formula  $2\text{Al}^{\text{FeCy}}.3\text{FeCy}$ , or  $(\text{Al})^{\text{FeCy}}_2$  (calc. 14.70 aluminium, and 22.53 iron), which is that of a prussian blue (p. 329) in which part of the iron (that which enters as *ferricum*) is replaced by an equivalent quantity of aluminium. (C. Tissier, Compt. rend. xlv. 232.)

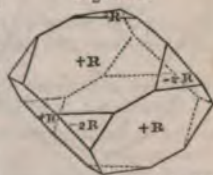
**FERROCYANIDE OF AMMONIUM**,  $(\text{NH})^{\text{FeCy}} + 3\text{aq.}$ , is obtained by saturating ferroproussic acid with ammonia, or by decomposing ferrocyanide of lead with carbonate of ammonia, and precipitating the filtered solution with alcohol, as the salt would be decomposed by evaporation. It forms pale yellow, transparent, octahedral crystals of the dimetric system, isomorphous, or rather homeomorphous, with ferrocyanide of potassium. Ordinary combination P. oP. Length of principal axis = 1.789. Inclination of P : P in the terminal edges =  $97^{\circ} 46'$ ; in the lateral edges =  $136^{\circ} 52'$ . They are permanent in the air, very soluble in cold water, insoluble in alcohol.

The solution of this salt mixed with chloride of ammonium and concentrated, yields rhombohedral crystals of *Chloroferrocyanide of ammonium*,  $(\text{NH})^{\text{FeCy}}.2\text{NH}^{\text{Cl}} + 3\text{aq.}$ , which are transparent, with a yellowish colour and glassy lustre, permanent in the air and very soluble in water. The crystals are sometimes rhombohedrons R, sometimes in the form of the next acuter rhombohedron,  $-2\text{R}$ , sometimes exhibiting the combination R. oR.  $-2\text{R}$  (fig. 360). Length of principal axis for R = 1.0325. Inclination of the faces R : R, forming the terminal edges of the hexagonal pyramid, =  $96^{\circ} 52'$ ; R : oR =  $129^{\circ} 59'$ ; R :  $-2\text{R}$  =  $126^{\circ} 59'$ ;  $-2\text{R}$  : oR =  $112^{\circ} 45'$ . The solution is decomposed by boiling, and deposits cyanide of iron. (Bunsen.)

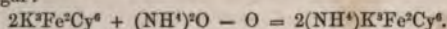
The analogous compound, *Bromo-ferrocyanide of ammonium*,  $(\text{NH})^{\text{FeCy}}.2\text{NH}^{\text{Br}} + 3\text{aq.}$  likewise forms rhombohedral crystals permanent in the air and very soluble in water. They exhibit the same faces as those of the preceding compound, but with different inclinations, the rhombohedron  $-2\text{R}$  also predominating. Length of principal axis for R = 0.9858. Inclination of R : R in the terminal edges =  $98^{\circ} 49'$ ;  $-2\text{R}$  :  $-2\text{R}$  =  $75^{\circ} 5'$ . (Himly and Bunsen, Pogg. Ann. xxxviii. 208.)

*Ferrocyanide of Ammonium and Potassium*,  $(\text{NH})^{\text{FeCy}}. \text{K}^{\text{FeCy}}$ .—Obtained by the action

Fig. 360.

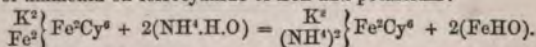


of ammonia on ferrieyanide of potassium in presence of reducing agents, such as grape- or milk-sugar:



The ammonia should be poured on a mixture of about 20 pts. ferrieyanide of potassium to 1 pt. sugar; the mixture left to stand for some days in a loosely stoppered bottle and frequently shaken; and when its colour has changed to a pure yellow, the salt should be precipitated by alcohol and recrystallised from water, as it is liable to decompose if evaporated in presence of the reducing agent. The salt forms pale yellow square prisms, easily soluble in cold, and still more in hot water. When heated, it gives off hydrocyanic acid and cyanide of ammonium. With metallic salts it yields the same precipitates as ordinary yellow prussiate. Heated with fixed alkalis, it gives off ammonia and yields salts of similar constitution; *e. g.* with soda, the salt  $K^2NaFe^2Cy^6$ . (Reindel, J. pr. Chem. lxx. 450.)

Another ferrocyanide of ammonium and potassium,  $(NH^4)^2K^2Fe^2Cy^6$ , is obtained by decomposing the corresponding barium-salt,  $Ba^2K^2Fe^2Cy^6$ , with sulphate of ammonium; or by action of ammonia on ferrocyanide of iron and potassium:



(Reindel, J. pr. Chem. lxxvi. 342.)

**Ferrocyanide of Barium**,  $Ba^2Fe^2Cy^6 + 6 aq.$ —Obtained by saturating ferrous prussic acid with baryta-water or carbonate of barium; by decomposing prussian blue with baryta-water at the boiling heat, filtering at the same temperature and leaving the solution to crystallise; or by decomposing a solution of ferrocyanide of potassium with chloride of barium at the boiling heat, the latter being used in considerable excess (more than 2 at. chloride of barium to 1 at. of the yellow prussiate), and again boiling the crystalline powder which separates on cooling, with chloride of barium. If the chloride of barium is not present in considerable excess, a double ferrocyanide of barium and potassium is produced.

Ferrocyanide of barium may also be produced by the action of ferrous sulphate on cyanide of barium ( $6BaCy + Fe^2SO^4 = Ba^2Fe^2Cy^6 + Ba^2SO^4$ ), which, according to Margueritte and De Sourdeval (p. 203), may easily be obtained by passing a current of air over an ignited mixture of charcoal and carbonate of barium. If this process should fulfil the expectations of its authors, ferrocyanide of barium may take the place of the potassium-salt for the preparation of certain ferrocyanides used in the arts, being easily converted into ferroproussic acid by the action of dilute sulphuric acid, into prussian blue by ferric salts, &c.

Ferrocyanide of barium crystallises in flattened, oblique, rectangular, monoclinic prisms, yellow, non-efflorescent, soluble in 584 pts. of cold and 116 pts. of boiling water (Duflos). At  $40^\circ C.$  they give off  $\frac{1}{12}$  of their water, and become white and opaque, the remaining  $\frac{1}{12}$  not being evolved till the salt begins to decompose. At a red heat, it gives off nitrogen, and leaves a mixture of carbide of iron and carbide of barium, or, if in contact with the air, a mixture of ferric oxide and carbonate of barium. On passing chlorine through the aqueous solution, it becomes turbid, acquires a greenish-yellow colour, deposits a green powder, then becomes brown and dark-red, and is decomposed by evaporation, depositing a bluish-white powder, but no crystals.

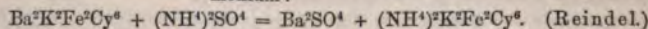
Fig. 361.



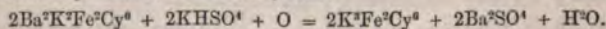
**Ferrocyanide of Barium and Potassium**,  $(Ba^2K^2)Fe^2Cy^6 + 3 aq.$ , is produced by mixing the boiling concentrated solutions of 2 pts. ferrocyanide of potassium and 1 pt. chloride of barium, and crystallises on cooling in small, light-yellow rhombohedrons, truncated by the face *oR*. Length of principal axis = 1.670. Inclination of *R* : *R* in terminal edges =  $98^\circ 33'$ ; *R* : *oR* =  $118^\circ 53'$ .

The crystals dissolve in 38 pts. of cold and 9.5 pts. of boiling water.

By treating the solution of this salt with soluble sulphates, a number of other double ferrocyanides containing potassium may be obtained; thus, with sulphate of ammonium:



The acid sulphates of the alkali-metals, in presence of an oxidising substance, convert it into ferrieyanides of alkali-metal, thus:



(Reindel, J. pr. Chem. lxxvi. 342.)

**FERROCYANIDE OF BISMUTH.**—Nitrate of bismuth forms with ferrocyanide of potassium a white, yellowish-white, or yellow precipitate, which afterwards turns green. It dissolves in nitric acid, and is precipitated therefrom by water.

**FERROCYANIDE OF CADMIUM** is a white precipitate soluble in ammonia.

**FERROCYANIDE OF CALCIUM**,  $\text{Ca}^2\text{Fe}^2\text{Cy}^4 + 12 \text{ aq.}$ , obtained by boiling prussian blue with milk of lime not in excess, evaporating the filtrate to a syrup, and leaving it to crystallise, forms large flattened rhombic prisms, of a light yellow colour, very bitter and disagreeable taste, very soluble in water, insoluble in alcohol.

Prussian blue, boiled or digested with excess of lime, yields basic compounds, or oxyferrocyanides of calcium, (Gm. vii. 482.)

**Ferrocyanide of Calcium and Potassium**,  $(\text{Ca}^2\text{K}^2)\text{Fe}^2\text{Cy}^4 + 3 \text{ aq.}$ , is obtained as a yellowish-white crystalline precipitate on adding ferrocyanide of potassium to a solution of a calcium-salt, not too dilute.

**FERROCYANIDE OF CERIUM.**—White precipitate.

**FERROCYANIDE OF COBALT**,  $\text{Co}^2\text{Fe}^2\text{Cy}^4$ .—Pale blue hydrated precipitate, which, when carefully heated, gives off the greater part of its water, and assumes a dark green colour. If it be then heated to  $360^\circ \text{C.}$ , it becomes light green, giving off water and a small quantity of cyanide of ammonium. When more strongly heated in a close vessel, it gives off nitrogen, and leaves a mixture of the carbides of iron and cobalt, which glows when raised to a higher temperature. The compound dissolves easily in strong sulphuric acid, forming a red liquid, which, after some time, deposits *sulphate of ferrocyanide of cobalt*, as a rose-coloured, crystalline powder, which is decomposed by water (Berzelius). Ferrocyanide of cobalt dissolves in ammonia and in carbonate of ammonia (Wittstein), not in sal-ammoniac. (Brett.)

**FERROCYANIDES OF COPPER.** *Cuprous Ferrocyanide*,  $\text{CuCu}^2\text{Fe}^2\text{Cy}^4$ .—Ferrocyanide of potassium added to a solution of cuprous chloride in hydrochloric acid, throws down white flakes, which, when exposed to the air, or to the action of chlorine-water, become purple-red, and are converted into cupric ferrocyanide (Proust). Cuprous ferrocyanide is likewise obtained by the action of acids on the following compound (Schulz). It dissolves in ammonia, but not in ammoniacal salts. (Wittstein.)

*Potassio-cuprous Ferrocyanide*,  $\text{Cu}^2\text{K}^2\text{Fe}^2\text{Cy}^4 + 3 \text{ aq.} = \frac{\text{CuCu}^2}{\text{K}_2}\text{Fe}^2\text{Cy}^4 + 3 \text{ aq.}$ —

When precipitated cupric ferrocyanide is added to a solution of cyanide of potassium, cyanogen is evolved, and a light yellow solution is formed, which, if the cyanide of potassium is not in excess, deposits, first a deep red precipitate, and after filtration, small square prismatic crystals, of a dark red-brown colour, and having the composition indicated by the above formula. This compound is more easily obtained by dropping a solution of cupric sulphate into a mixture of cyanide and ferrocyanide of potassium, then heating the liquid and leaving it to itself. The crystals give off water at  $100^\circ \text{C.}$  and turn black; they are insoluble in water, ether, and alcohol, but soluble in cyanide of potassium. Boiling water decomposes them, with formation of ferrocyanide of potassium. Acids also decompose them, separating white cuprous ferrocyanide. (C. Schulz, J. pr. Chem. lxxviii. 257.)

*Cyanide of Potassium, Cuprous and Ferrous*,  $(\text{K}^2\text{Cu}^2\text{Fe}^2)\text{Cy}^4 + 4 \text{ aq.}$ —A liquid consisting of cyanide of potassium and sulphate of copper containing iron, which had been used for coppering by electrolysis, and had stood for a long time in an imperfectly closed vessel, was found to have deposited brown-red octahedral crystals, resembling chrome-alum, and agreeing in composition with the above formula. The same salt was obtained, in the form of a chocolate-coloured powder, by boiling cuprous cyanide with solution of ferrocyanide of potassium, and leaving the liquid to cool. (Bolley and Moldenhauer, Ann. Ch. Pharm. cvi. 228.)

According to Moldenhauer's analysis, the crystals contain 4 at. water; according to W. J. Wonfor (Chem. Soc. J. xv. 357), they contain 5 at. water, and have the form of the cubo-octahedron (fig. 176, p. 124).

[For Kuhn's experiments on the action of ferrocyanide and ferricyanide of potassium on the oxides, sulphides, and cyanides of copper, see Ann. Ch. Pharm. lxxxvii. 127.]

*Cupric Ferrocyanide*,  $\text{Cu}^2\text{Fe}^2\text{Cy}^4$ .—Ferrocyanide of potassium added to excess of a cupric salt forms a dark purple-red precipitate. The liquids, if concentrated, solidify in a magma when stirred; if more dilute, they yield thick flakes; and if very dilute, the mixture assumes a beautiful red colour. This precipitate, even when a large excess of copper-salt is used, carries down with it a large quantity of ferrocyanide of potassium, which cannot be removed by washing. If, therefore, the precipitate be suspended in water, and decomposed by sulphuretted hydrogen—which takes a long time—a strongly acid liquid is obtained which, like ferropussian acid, deposits prussian blue on exposure to the air, and forms a blue precipitate with



ferric salts, but is not precipitated by ether, except on addition of hydrochloric acid. It contains  $H^+KFe^6Cy^{12}$  (Williamson, Ann. Ch. Pharm. lvii. 245). According to Rammelsberg (Pogg. Ann. lxxiv. 65), acetate or sulphate of copper mixed with ferropurssic acid yields pure ferrocyanide of copper, which, after drying over sulphuric acid, contains  $Cu^+Fe^2Cy^6 + 7 \text{ aq.}$ ; according to Monthiers, however, it contains  $Cu^+Fe^2Cy^6 + 9 \text{ aq.}$

The salt gives up only a part of its water when gently heated, and at a stronger heat evolves hydrocyanate of ammonia as well as water (Vauquelin), also carbonate of ammonia and nitrogen gas (Berzelius). The residue, if more strongly heated in a retort, exhibits a faint glow, and appears afterwards to be composed of 1 at. bicarbonate of iron and 2 at. monocarbide of copper (Berzelius). Aqueous potash decomposes the salt, producing ferrocyanide of potassium and hydrated cupric oxide (Ittner). In oil of vitriol, which dissolves but little of it, the salt assumes a greenish yellow-white colour; but on subsequent immersion in water, which withdraws the sulphuric acid, it resumes its dark red colour (Berzelius). It is insoluble in water and in acids, which do not decompose it; also insoluble in ammoniacal salts, (Brett, Wittstein.) It dissolves, however, in aqueous ammonia, forming a colourless solution, which, on evaporation leaves the cupric ferrocyanide with its original colour. This reaction affords the means of detecting extremely small quantities of copper, even when associated with other metals. (Warington. See p. 56.)

*Diammonio-cupric Ferrocyanide*,  $4NH^3.Cu^+Fe^2Cy^6 + \text{aq.}$ , or *Ferrocyanide of Cuprammonium*,  $(NH^3Cu)^4.Fe^2Cy^6 + \text{aq.}$ —Produced by adding ferrocyanide of potassium to a solution of nitrate of cuprammonium (or of any cupric salt containing sufficient ammonia to form a clear solution). It is a pale yellow crystalline precipitate, soluble in free ammonia, insoluble in water or alcohol. Dilute acids withdraw the ammonia, leaving red-brown cupric ferrocyanide, (Monthiers, J. Pharm. [3] xi. 249; Bunsen, Pogg. Ann. xxxiv. 134.)

*Octammonio-cupric Ferrocyanide*,  $8NH^3.Cu^+Fe^2Cy^6$ , or *Ferrocyanide of Ammonio-cuprammonium*,  $[N.H^3(NH^3)Cu]^4.Fe^2Cy^6$ .—Cupric ferrocyanide, or the preceding ammonio-compound in the moist state, absorbs ammoniacal gas, assuming a green colour and being converted into the octammonio-compound. The latter is very unstable, turning yellow and giving off half its ammonia on exposure to the air. (Monthiers.)

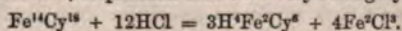
*Potassio-cupric Ferrocyanide*,  $Cu^2K^2Fe^2Cy^6$ .—Produced, according to Mosander, by adding a cupric salt, drop by drop, to excess of ferrocyanide of potassium. [According to Rammelsberg, however, (Pogg. Ann. lxxiv. 65), the precipitate thus formed contains water and is composed according to the improbable formula  $Cu^+Fe^2Cy^6.K^2Fe^2Cy^4 + 2 \text{ aq.}$  When, on the other hand, the ferrocyanide is dropped into excess of the cupric salt, the precipitate has the composition  $2(Cu^2K^2Fe^2Cy^6, \text{ aq.}) + 9(Cu^+Fe^2Cy^6, 7 \text{ aq.})$  Jahresber. d. Chem. 1847-8.]

The compound  $Cu^2K^2Fe^2Cy^6$  also constitutes the dark red precipitate mentioned as produced in the preparation of potassio-cuprous cyanide, when a comparatively small quantity of cyanide of potassium is used. (Schulz.)

The corresponding *sodium* and *ammonium* compounds are obtained in like manner. The latter,  $Cu^2(NH^3)^2Fe^2Cy^6$ , is a scarlet crystalline body, which turns brown on drying. (Schulz.)

**Ferrocyanide of Ethyl**,  $(C^2H^3)^4Fe^2Cy^6$ .—When hydrochloric acid gas is passed into a well cooled alcoholic solution of ferropurssic acid, colourless crystals are obtained which, after drying for a certain time over lime, consist of  $(C^2H^3)^4Fe^2Cy^6 + 2C^2H^3Cl + 6 \text{ aq.}$  Their concentrated alcoholic solution, mixed with ether, deposits nacreous crystals of pure ferrocyanide of ethyl,  $(C^2H^3)^4Fe^2Cy^6 + 6 \text{ aq.}$  Both compounds become anhydrous by continued exposure over lime. The corresponding *methyl* and *amyl*-compounds appear also to exist. (H. Buff, Ann. Ch. Pharm. xci. 253.)

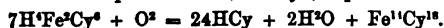
**Ferrocyanide of Hydrogen**. *Ferropurssic* or *Hydroferrocyanic acid*,  $H^+Fe^2Cy^6 = 4HCy.2FeCy$ . *Ferruretted Chyazic acid*. *Eisenblausäure*, *Wasserstoffeisencyanür*, *Ferrocyanwasserstoffsäure*. This acid, discovered by Porrett (Phil. Trans. 1814, p. 527), is obtained by decomposing ferrocyanide of barium with sulphuric acid, ferrocyanide of potassium with tartaric acid, ferrocyanide of lead or copper with sulphydric acid, or prussian blue with very strong hydrochloric acid;



A good method of preparing it is to dissolve ferrocyanide of potassium in a small quantity of water, boil the solution to expel the air, leave it to cool in a stoppered bottle, then mix it with strong hydrochloric acid, also freed from air, and shake up the liquid with ether. The ferropurssic acid is then precipitated in thin white scales, which may be collected on a filter, washed with ether-alcohol, pressed, and dried in vacuo over sulphuric acid (Posselt, Ann. Ch. Pharm. xlii. 163). It is better to separate the

acid from its solution by precipitation with ether than by evaporation, as the solution decomposes when exposed to the air. If the aqueous solution of ferrocyanide of potassium be mixed, first with ether, and then with hydrochloric acid, the ferroproussic acid separates perfectly white, and may be dried without becoming coloured. It may then be further purified by pressure, solution in alcohol, and precipitation with ether (Dollfus). Kuhlmann prepares ferroproussic acid on the large scale by decomposing ferrocyanide of barium with an equivalent quantity of sulphuric acid. The clarified solution is preserved in well closed stone-ware jars and sent in that state into the market.

Ferroproussic acid crystallises in white grains or small interlaced needles: larger crystals are deposited from an alcoholic solution covered with a layer of ether. It is easily soluble in water and alcohol, insoluble in ether. When exposed to the air, it absorbs oxygen, even at ordinary temperatures, and more quickly when heated, hydrocyanic acid being set free and prussian blue,  $\text{Fe}^{\text{II}}\text{Cy}^{\text{II}}$ , deposited:



(Reiman and Carius, Ann. Ch. Pharm. cxiii. 39.)

This reaction is applied to the production of prussian blue in calico-printing. The pattern is printed with a mixture of ferrocyanide of potassium with tartaric acid, or with sulphuric acid and alum, and exposed to the action of a hot steam-bath. In this treatment, ferroproussic acid is first set free, and then decomposed in the manner just explained.

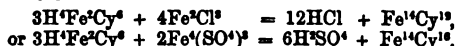
Ferroproussic acid is a strong acid, having a sour taste, reddening litmus, and decomposing carbonates and acetates without the aid of heat: it even decomposes tartrates and oxalates. With most metallic salts it acts in the same manner as ferrocyanide of potassium. Heated with mercuric oxide, it yields cyanide of mercury and protocyanide of iron:



but the ferrous cyanide is immediately oxidised by the excess of mercuric oxide, with separation of metallic mercury.

Ferroproussic acid is tetrabasic, as appears from the constitution of some of the double ferrocyanides; e. g.  $\text{K}^2(\text{NH}^{\text{I}})^2\text{Fe}^{\text{II}}\text{Cy}^{\text{I}}$ , and from the relations between the ferrous and ferricyanides (p. 222).

**FERROCYANIDE OF IRON. FERRIC FERROCYANIDE.**  $\text{Fe}^{\text{III}}\text{Cy}^{\text{I}} + 9 \text{ aq.}$ , or rather  $\text{Fe}^{\text{III}}\text{Cy}^{\text{I}} + 18 \text{ aq.} = (\text{Fe}^{\text{III}})^{\text{I}}\text{Fe}^{\text{II}}\text{Cy}^{\text{I}} + 18 \text{ aq.} = \text{Fe}^{\text{II}}\text{Fe}^{\text{III}}\text{Cy}^{\text{I}} + 6 \text{ aq.}$ \*—This is one of the compounds designated by the common name of Prussian blue. It is obtained in the pure state by precipitating ferroproussic acid with a ferric salt:



The same precipitate is formed by adding ferrocyanide of potassium to a ferric salt, the latter being in excess; it always carries down with it a certain quantity of the alkaline ferrocyanide, which, however, may be removed by digestion with the ferric salt and subsequent washing. If, on the contrary, the ferric salt be added to excess of the alkaline ferrocyanide, a much larger quantity of the latter is carried down with the precipitate, and cannot be completely separated by any amount of washing (p. 229).

The pure ferric ferrocyanide obtained as above is sometimes called *Paris blue*.

Ferric ferrocyanide is likewise produced by the following reactions

a. By precipitating a ferroso-ferric salt with cyanide of potassium:



if the iron-solution contains a larger proportion of ferric salt, the excess of the latter does not appear to alter the character of the precipitate; but if the ferrous salt is in excess, the precipitate will have a different character, approaching to the composition of ferrous ferricyanide, or Turnbull's blue. (See FERRICYANIDES.)

b. By mixing hydrocyanic acid, first with potash, then with a ferroso-ferric salt, and then with excess of hydrochloric acid. In this case, ferrocyanide of potassium is first formed, and this with the ferric salt present forms prussian blue. This is one of the chief tests for hydrocyanic acid (p. 218).

c. By immersing recently precipitated ferroso-ferric hydrate in hydrocyanic acid.

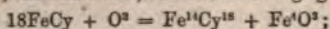
d. By immersing ferrous cyanide in a solution of a ferric salt, which is thereby reduced to a ferrous salt:



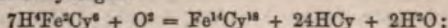
$$* \text{Fe} = \text{Fe}^2 = 56; \text{Fe} = \frac{1}{2}\text{Fe} = 18\frac{1}{2}.$$



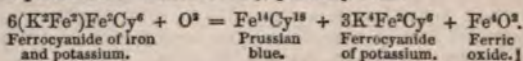
a. By the action of air, chlorine-water, or other oxidising agents, on ferrous cyanide:



or, on ferrocyanide of hydrogen:



or, on ferrocyanide of iron and potassium (the white precipitate formed by adding ferrocyanide of potassium to a ferrous salt), probably thus:



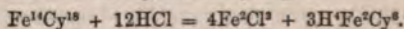
It is chiefly by this last reaction that prussian blue is prepared on the large scale, ferrocyanide of potassium being first precipitated by ferrous sulphate, and the resulting white or light blue precipitate either left to oxidise by contact with the air, or subjected to the action of nitric acid, chlorine, hypochlorites, chromic acid, &c. The product, however, is not pure ferric ferrocyanide: for it is certain that another and simpler reaction takes place at the same time, by which the ferrocyanide of iron and potassium is converted, by the abstraction of 1 at. potassium, into ferricyanide of iron and potassium,  $\text{K} \left\{ \text{Fe}^2\text{Cy}^6 \right\}$ , which also possesses a fine deep blue colour. Commercial prussian blue is therefore generally a mixture of this compound with ferric ferrocyanide,  $\text{Fe}^4\text{Cy}^6$ , the one or the other predominating according to the manner in which the process is conducted. (See PRUSSIAN BLUE.)

Ferric ferrocyanide forms, when dry, a dark blue mass, having a strong coppery lustre and conchoidal fracture. It cannot be dehydrated by heat, as it is thereby decomposed, giving off hydrocyanic acid and leaving ferric oxide. Heated in contact with the air, it takes fire and burns like tinder, leaving ferric oxide.

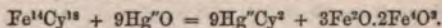
It is insoluble in water, alcohol, ether, and oils, and is neither dissolved nor decomposed by dilute mineral acids. It dissolves with violet colour in *tartrate of ammonia*, and with blue colour in *oxalic acid*. This latter solution may be used as a blue ink; it is prepared by triturating prussian blue with 1 or 2 pts. of crystallised oxalic acid and a small quantity of cold water till it forms a thick paste, which may be dissolved in a large quantity of water.

Immersed in cold strong *sulphuric acid*, it is converted into a white pasty mass, without evolving hydrocyanic acid or giving up iron; the addition of water, alcohol, or even ether, restores the blue colour without contact with the air (Robiquet). The white pasty mass does not dissolve in excess of sulphuric acid; when dried in *vacuo* on a porous tile, it leaves a white pasty amorphous powder called *sulphate of prussian blue*, which is immediately decomposed by water into prussian blue and dilute sulphuric acid. (Berzelius.)

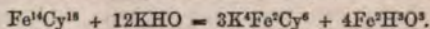
Strong nitric or sulphuric acid heated with ferric ferrocyanide decomposes it by oxidation. Strong hydrochloric acid gradually decomposes it, abstracting the iron in the form of ferric chloride, and the residue, if continually treated with fresh quantities of acid, ultimately consists of ferrocyanide of hydrogen:



*Chlorine-water* converts ferric ferrocyanide into a green compound, which turns blue in contact with ferrous or stannous chloride. Ferric ferrocyanide boiled with *mercuric oxide* yields cyanide of mercury and ferroso-ferric oxide:

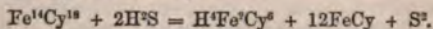


The *fixed alkalis*, and *magnesia*, in presence of water, decompose ferric ferrocyanide, especially with aid of heat, forming an alkaline ferrocyanide and ferric hydrate:



The *carbonates of potassium and sodium* act in a similar manner, but less powerfully. *Ammonia* at first unites with ferric ferrocyanide, but afterwards decomposes it, forming a greyish-brown basic compound, which again yields prussian blue when treated with acids. *Lime* also boiled with ferric ferrocyanide forms a similar basic compound, but of a light yellow colour.

Aqueous *sulphydric acid* decomposes ferric ferrocyanide, forming ferrous cyanide and ferroprussic acid, with separation of sulphur:



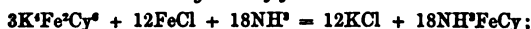
*Iron or tin filings* placed in contact with it under water, withdraw part of the



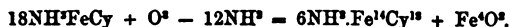
cyanogen and convert it into white ferrous cyanide. *Cuprous chloride* also turns it white. Boiled with a *polysulphide of potassium*, it yields, according to Porrett, sulphocyanate of potassium, a sulphide of iron being probably formed at the same time; e.g.  $\text{Fe}^{\text{I}}\text{Cy}^{\text{III}} + 9\text{K}^{\text{I}}\text{S}^{\text{II}} = 18\text{K}^{\text{I}}\text{CyS} + \text{Fe}^{\text{I}}\text{S}^{\text{II}}$ .

*Soluble Prussian blue.*—When ferric chloride is added to excess of ferrocyanide of potassium, a dark-blue precipitate is formed, which is insoluble in the saline liquid, but gradually dissolves during washing, the water acquiring a blue colour, which becomes deeper as the soluble salts are removed. This precipitate contains potassium, which, indeed, is found both in the wash-waters and in the residue, even after the washing has been continued long enough to dissolve out a considerable portion of the precipitate. This is the soluble prussian blue of Berzelius and Robiquet; it is usually regarded as ferric ferrocyanide, retaining a certain and sometimes a considerable quantity of yellow prussiate, which is gradually dissolved out during the washing, and renders the precipitate also soluble (Gm. vii. 440). Kekulé, however (*Lehrbuch d. org. Chem.* i. 327), considers it improbable that this should be the case, seeing that a larger quantity of the yellow prussiate renders the precipitate insoluble. He considers it more probable that the precipitate consists of ferricyanide of iron and potassium ( $\text{KFe}^{\text{III}}\text{Fe}^{\text{II}}\text{Cy}^{\text{I}}$ ). The greatest degree of solubility is said to be obtained by precipitating 1 at. ferrocyanide of potassium with a solution of ferric iodide containing 1 at. or rather more of iodine. (Wagner's *Jahresbericht d. Chem. Technologie*, 1858, iv. p. 194.)

*Ammonio-ferric Ferrocyanide*,  $6\text{NH}^{\text{I}}\text{Fe}^{\text{I}}\text{Cy}^{\text{II}} + 9\text{H}^{\text{I}}\text{O}$ , or *Ferrocyanide of ferricum* and *ferricammonium*  $2\left(\text{NH}^{\text{I}}_{\text{Fe}}\right)\text{FeCy}^{\text{I}} + 3\text{H}^{\text{I}}\text{O}$ .—This, according to Monthiers (*J. Pharm.* [3] ix. 26), is the first product of the action of ammonia on ferric ferrocyanide, the ultimate products being, as already observed, ferric oxide and ferrocyanide of ammonium. The best mode of preparing it is to pour an excess of ammonia into a solution of protochloride of iron, and throw the whole on a filter resting in a funnel, the neck of which dips into a solution of ferrocyanide of potassium. As soon as the two liquids mix, a perfectly white precipitate is formed, which turns blue in contact with the air. This precipitate is digested with tartrate of ammonia, to remove the ferric oxide likewise produced in the reaction, the whole being kept for some hours at a temperature of  $60^{\circ}$  to  $80^{\circ}\text{C}$ ., and the precipitate then washed with distilled water. The first product formed is white *cyanide of ferrosammonium*:



and this when exposed to the air, takes up oxygen, gives off ammonia, and is converted into ammonio-ferric ferrocyanide and ferric oxide:



It is a blue powder with a tinge of violet. It begins to give off prussic acid at  $100^{\circ}\text{C}$ ., but retains its colour up to  $160^{\circ}$ , below which temperature no ammonia is evolved. It is altogether more stable than ferric ferrocyanide, not being attacked by tartrate of ammonium either at ordinary or at higher temperatures. (Monthiers.)

*Potassio-ferrous Ferrocyanide*,  $\text{K}^{\text{I}}\text{Fe}^{\text{I}}\text{Cy}^{\text{I}} = \left(\text{K}^{\text{I}}\right)\text{Fe}^{\text{I}}\text{Cy}^{\text{I}}$ .—This is the white (or yellow) insoluble substance formed when ferrocyanide of potassium is distilled with dilute sulphuric acid for the preparation of hydrocyanic acid (Everitt, *Phil. Mag.* [3] vi. 97):



It is also produced on adding ferrocyanide of potassium to a solution of a ferrous salt



the reaction consisting simply in an interchange between 2 at. iron (ferrous), and 2 at. potassium. If the ferrous salt is quite free from ferric salts, and the air is completely excluded, the precipitate is white, but it quickly turns blue in contact with the air. The solution of ferrous sulphite and hyposulphite obtained by immersing clean iron wire in aqueous sulphurous acid contained in a closed vessel, gives with ferrocyanide of potassium a perfectly white precipitate.

By the action of the air, nitric acid, and other oxidising agents, potassio-ferrous ferrocyanide is converted partly into ferricyanide of iron and potassium (Williamson), partly into ferric ferrocyanide. (See p. 228.)

*FERROCYANIDE OF LEAD*,  $\text{Pb}^{\text{I}}\text{Fe}^{\text{I}}\text{Cy}^{\text{I}} + 3\text{aq.}$ , is obtained as a white precipitate on mixing the solutions of nitrate of lead and ferrocyanide of potassium. It gives off all

its water when gently heated. The anhydrous salt ignited in a close vessel gives off nitrogen, and leaves a mixture of carbide of lead and carbide of iron, which burns like tinder when gently heated in contact with the air. The hydrated salt suddenly exposed to a strong heat, gives off water, carbonic acid, and cyanide of ammonium. The salt is decomposed by dilute sulphuric acid, and by aqueous sulphydric acid, yielding ferroproussic acid. Heated in sulphydric acid gas, it is resolved into sulphide of lead, sulphide of iron and hydrocyanic acid (Berzelius). It is insoluble in water, partially soluble in hot aqueous ammonia, perfectly soluble in a hot solution of chloride or succinate of ammonium, insoluble in other ammoniacal salts. (Wittstein.)

**FERROCYANIDE OF MAGNESIUM**,  $Mg^4Fe^2Cy^6 + 12 aq.$ , is obtained in the form of small, pale yellow, stellate needles, permanent in the air, by saturating ferroproussic acid with carbonate of magnesium, and evaporating the filtrate.

*Ferrocyanide of Magnesium and Ammonium* is obtained in an impure state by adding ferrocyanide of potassium, or of calcium, to a solution of a magnesium-salt containing sal-ammoniac and free ammonia. On boiling the liquid, the double salt is deposited in the form of a white powder, which does not decompose at  $100^\circ C$ .

*Ferrocyanide of Magnesium and Potassium*,  $(Mg^2K^2)Fe^2Cy^6$ , is obtained as a white granular precipitate on adding ferrocyanide of potassium in excess to a not very dilute solution of a magnesium-salt.

**FERROCYANIDE OF MANGANESE**.—White precipitate, soluble in hydrochloric acid. When a solution of a manganous salt is poured into excess of ferrocyanide of potassium, the precipitate contains both manganese and potassium.

**MERCURIC FERROCYANIDE**.—White precipitate obtained by adding ferrocyanide of potassium to solution of mercuric chloride.

*Ammonio-mercuric Ferrocyanide*,  $2NH^3(Hg^{''})^2Fe^2Cy^6 + aq.$ , or *Ferrocyanide of Mercury and Mercurammonium*,  $\left. \begin{matrix} N^2H^2Hg^{''} \\ Hg^{''} \end{matrix} \right\} Fe^2Cy^6 + aq.$ , is obtained by dissolving nitrate of mercurammonium (ammonio-mercuric nitrate) in a moderately strong solution of nitrate of ammonium containing free ammonia and cooled by ice, and precipitating with ferrocyanide of potassium. It forms wine-yellow rhomboidal prisms, which give off their ammonia on exposure to the air. They are decomposed by water, yielding cyanide of mercury, ferric oxide, and ammonia. If the solution of nitrate of ammonia used in the preparation is too strong or too hot, mercury is reduced, and if it is too dilute, the product is immediately decomposed by the water present. (Bunsen, Pogg. Ann. xxxiv. 139.)

**FERROCYANIDES OF MOLYBDENUM**.—Ferrocyanide of potassium forms with molybdous salts, a dark-brown precipitate soluble in excess of the reagent and in ammonia; with molybdic salts, also a dark brown precipitate, insoluble in excess of the alkaline ferrocyanide, but soluble with decomposition in ammonia; with solutions of molybdic acid in the stronger acids, it forms a red-brown precipitate, soluble in excess of the ferrocyanide, and in ammonia, with formation of ferrocyanide and molybdate of ammonium. (Berzelius.)

**FERROCYANIDE OF NICKEL**,  $Ni^2Fe^2Cy^6$ .—Precipitated in pale apple-green flocks, soluble with red colour in ammonia, insoluble in ammoniacal salts. When thus prepared, it always retains ferrocyanide of potassium, which cannot be removed by washing. It may, however, be obtained quite pure by decomposing the following compound with boiling water.

*Ammonio-ferrocyanide of Nickel*,  $10NH^3.Ni^2Fe^2Cy^6 + 4 aq.$ —A solution of recently precipitated ferrocyanide of nickel in excess of ammonia deposits this compound, after a short time, in a multitude of very delicate violet-coloured needles. The same compound is obtained by adding ferrocyanide of potassium to a nickel-salt containing a large excess of ammonia. In the moist state, it is decomposed by mere exposure to the air, giving off ammonia and water and leaving ferrocyanide of nickel; but after drying, it bears a heat of  $100^\circ$ — $150^\circ C$ . without decomposing. Boiling with water also decomposes it, the ammonia dissolving and ferrocyanide of nickel remaining. (Reynoso, Ann. Ch. Phys. [3] xxx. 252.)

*Ferrocyanide of Nickel-ammonium*,  $(NH^3Ni)^4Fe^2Cy^6 + 4 aq.$ , is obtained as a greenish white precipitate on adding ferrocyanide of potassium to a solution of nitrate of nickel-ammonium. It is insoluble in water and more stable than the preceding. (Reynoso.)

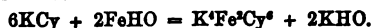
**FERROCYANIDE OF POTASSIUM**,  $K^4Fe^2Cy^6 = 4KCy.2FeCy$ . *Prussiate of Potash*, *Ferroproussiate of Potash*, *Yellow Prussiate of Potash*, *Yellow Prussiate*, *Blood-lye-salt*, *Blutlaugensalz*, *Kaliumeisencyanür*. (Gentile, Dingl. polytechn. J. Ixi.

289; lxxvi. 352; xciv. 197; cxvii. 414.—Liebig, Ann. Ch. Pharm. xxxviii. 20. Habich, Dingl. cxl. 371.—Wagner's Jahresber. d. Chem. Technologie, 1856, p. 111. —Brunquell, Dingl. cxl. 374; cxli. 47; Wagner's Jahresber. 1856, p. 102.—Karm-rod, Dingl. cxlvi. 294; Wagner's Jahresber. 1857, p. 139.—Nöllner, Ann. Ch. Pharm. cviii. 8; Wagner's Jahresber. 1858, p. 175.—R. Hofmann, Dingl. cli. 63; Wagner's Jahresber. 1858, p. 179.—Graeger, Polyt. Centralhalle, 1858, pp. 26, 33, 49; Wagner's Jahresber. 1858, p. 183.—Handwörterbuch der Chemie, 2<sup>o</sup> Aufl. ii. [2] 184.—Gm. vii. 463.)

This important salt was first prepared about the middle of the last century by Macquer, who obtained it by the action of alkali on prussian blue, and called it *Phlogisticated alkali*. Sage, and afterwards Bergmann, showed that it might be prepared in the dry way. The iron contained in it was at first regarded as an impurity, till Berthollet showed that it was an essential constituent. The salt is now manufactured on a very large scale, and used for the preparation of cyanide and cyanate of potassium, prussic acid, prussian blue, and other cyanogen-compounds; also in dyeing and calico printing, for the direct formation of prussian blue on tissues.

*Formation.*—Ferrocyanide of potassium is formed on bringing together the following substances:

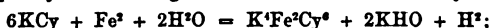
1. Protoxide of iron with aqueous cyanide of potassium.—2. Ferroproussic acid with hydrate or carbonate of potassium.—3. Ferrous hydrate with cyanide of potassium, potash being formed at the same time:



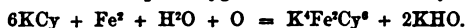
4. Ferrous cyanide with aqueous potash:



5. Ferric ferrocyanide or ferrous ferricyanide with aqueous potash, ferric oxide being separated in the first case (p. 228), and ferroso-ferric oxide in the second (p. 202).—6. By the action of potash on various ferrocyanides (p. 223).—7. By bringing metallic iron in contact with aqueous cyanide of potassium, the action taking place slowly at ordinary temperatures, quickly at the boiling heat. If the air is excluded, hydrogen is evolved:



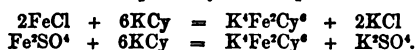
but if the air has access to the liquid, oxygen is absorbed and no hydrogen is evolved:



8. Sulphide of iron with aqueous cyanide of potassium, sulphide of potassium being formed at the same time:



9. Any soluble ferrous salt with aqueous cyanide of potassium:



*Preparation.*—1. *On the small scale*, pure ferrocyanide of potassium is easily obtained by adding pure Prussian blue (ferric ferrocyanide) to boiling aqueous potash, as long as its blue colour changes to brown, then filtering, and evaporating the liquid to the crystallising point. If commercial Prussian blue is used, the salt obtained will probably be contaminated with carbonate, sulphate, and other salts of potassium, and with green *prussiate of potash* (p. 235). It may be purified by picking out the crystals and recrystallising them several times, or, according to Berzelius, by heating the salt, first gently till it effloresces, afterwards to the melting point; dissolving it in water, which then leaves charcoal and carbide of iron undissolved; adding acetic acid to convert the carbonate and cyanide of potassium in the solution into acetate; precipitating the sulphuric acid present with solution of acetate of barium, added gradually and not in excess; then filtering, evaporating, precipitating the ferrocyanide of potassium by alcohol, and twice recrystallising it from hot water.

2. *On the large scale*, ferrocyanide of potassium is prepared by adding animal matters, such as horn, feathers, dried blood, leather-clippings, &c., mixed with iron filings, to fused carbonate of potassium (pearl-ash), lixiviating the fused mass with water, then filtering and crystallising by evaporation. The animal matter contains nitrogen and carbon, the latter in larger proportion than is required to form cyanogen with the nitrogen: hence when these substances are fused with carbonate of potassium, the excess of carbon reduces potassium from the carbonate, and the potassium thus set free unites with the cyanogen formed from the nitrogen and the remainder of the carbon, producing cyanide of potassium, which is converted into ferrocyanide in the subsequent lixiviation. It was formerly supposed that the cyanide of potassium is converted into,



ferrocyanide during the fusion, by the action of the iron present in the fused mass, and that, in the lixiviation, the ferrocyanide is simply dissolved out. This, however, is impossible, inasmuch as the ferrocyanide is decomposed at the temperature to which the mass is exposed, into cyanide of potassium, carbide of iron, and nitrogen (p. 199). Moreover, Liebig has shown that if the fused mass, soon after cooling, be lixiviated with aqueous alcohol (brandy), nothing but cyanide of potassium is dissolved out, and the residual mass treated with water no longer yields any ferrocyanide. The ferrocyanide obtained when the fused mass is treated with water in the usual way, does not exist ready formed in the mass, but is produced by the mutual action of the cyanide of potassium and the metallic iron existing therein; moreover the product is considerably increased by adding, during the lixiviation, more metallic iron, or sulphide of iron, or a soluble ferrous salt (p. 231). This view has indeed been called in question by Runge (Pogg. Ann. lxi. 96) and others, who have found that the melted mass, when treated with brandy, yields but little cyanide of potassium, but afterwards yields the usual quantity of ferrocyanide when lixiviated with water. These results were probably due to the use of alcohol of too great strength, which dissolves cyanide of potassium but slowly, or to the melted mass having been left for some time in contact with the air, in which case the highly deliquescent cyanide of potassium would absorb water, and ferrocyanide would be gradually formed. Liebig's view has been confirmed by the recent experiments of Nöllner and R. Hoffmann, who find that when the fused mass is left to cool slowly, pure cyanide of potassium often separates out of it. Hoffmann has also shown, that when pure cyanide of potassium mixed with iron is treated with acetic acid and alcohol, it is completely decomposed, without formation of ferrocyanide, and that the ferrocyanide itself is not decomposed by acetic acid and alcohol; now when the fused mass obtained in the manufacturing process is pulverised and heated with acetic acid and alcohol, it behaves like a mixture of iron and cyanide of potassium, and the residue treated with water no longer yields ferrocyanide of potassium.

The manufacture of ferrocyanide of potassium (yellow prussiate) consists of three stages: *a.* The preparation of the melted mass, technically called "metal;" *b.* The lixiviation; *c.* The crystallisation.

*a.* The "metal" is prepared by melting animal matters with pearlash, generally with addition of iron, sometimes, though less advantageously, without it. The animal substances used are horn, woollen rags, dried blood, carcases of animals, hairs, feathers, leather-clippings, old shoes, &c.; they are sometimes used in their original state, sometimes subjected to a previous dry distillation, the ammonia thereby evolved being condensed in hydrochloric or sulphuric acid, and thus obtained as a secondary product, and the residual azotised charcoal used for the preparation of the cyanide. Those substances are of course the most eligible which contain the largest proportion of nitrogen: in this respect, the several kinds of animal matter differ considerably, as shown by the following table given by Karmrodt.

100 parts of horn . . . .	contain 15 to 17 p. c. nitrogen.
" dried blood . . . .	15 " 17 "
" woollen rags . . . .	10 " 16 "
" sheep-shearings . . . .	16 " 17 "
" calves' hair . . . .	16 " 17 "
" bristles . . . .	9 " 10 "
" feathers . . . .	17 "
" hide-clippings . . . .	4 " 5 "
" old shoes . . . .	6 " 7 "
" charcoal from horn, according to the heat to which it has been subjected . .	2 " 7 "
" charcoal from rags . . . .	2 " 12 "

According to Boussingault and Payen, horn contains 14.3, air-dried muscular flesh 13.4, and woollen rags 16.0 p. c. nitrogen. According to Nöllner, old leather often contains not more than 1 to 2 p. c. nitrogen, whereas well preserved leather contains from 6 to 12 p. c.

The charcoal obtained by the carbonisation of animal substances contains nitrogen, but less in proportion as it has been more strongly heated; at the same time, however, the quantity of charcoal obtained is less. 100 parts of rags carbonised at a certain temperature, yielded 76 pts. charcoal containing 12 p. c. nitrogen, whereas the same rags charred at a stronger heat yielded 25 pts. charcoal containing only 1.25 to 2 p. c. nitrogen. It is important, therefore, not to heat the animal substances too strongly, and to stop the distillation at such a point that the yield of charcoal shall be from 50 to 70 p. c.

It is important that the animal substances used should not yield much ash, as this,

besides thickening the mass, will decompose a portion of the potash, converting it into soluble salts which will mix with the ferrocyanide: the animal substances should, therefore, be well-cleaned, especially from sand, before calcination (1 pt. of sand will decompose 2 pta. of pearl-ash).

The *potassium* for the preparation is supplied in the form of carbonate (pearl-ash). It is not necessary to use perfectly pure carbonate of potassium; indeed a certain proportion of sulphate is said to act beneficially, by forming sulphide of iron. According to Brunnequell and Hoffmann, however, it is always injurious, as it converts a portion of the cyanide of potassium into sulphide, cyanate, and sulphocyanate.

In localities where potash from plant-ashes is too dear, an impure carbonate is sometimes prepared from the sulphate by ignition with coal and carbonate of lime, just as, in the ordinary method of soda-making. The sulphate of potassium used for this purpose may be obtained from the mother-liquor of sea-water, and of the ashes of kelp and varechs. (See POTASH.) Bramwell uses, instead of carbonate of potassium, the sulphide obtained by igniting sulphate of potassium with charcoal. It is fused with animal matter and an equivalent quantity of iron, which is thereby converted into sulphide.

The addition of *iron* in the melting process might appear at first sight to be unnecessary, inasmuch as the conversion of the cyanide of potassium into ferrocyanide takes place only in the lixiviation. It is, however, required for two reasons: first, because the sulphate of potassium, which is almost always present, is converted, by ignition with charcoal, into sulphide and bisulphide of potassium, and the latter, if no iron is present, converts a portion of the cyanide of potassium into sulphocyanate, which is not converted into ferrocyanide in the subsequent lixiviation, and consequently occasions a loss of cyanogen; and, secondly, because the bisulphide of potassium exerts a very rapid corroding action on the iron pot in which the materials are fused. Now, when iron is added in the form of filings, turnings, &c., it easily decomposes the alkaline sulphides, thereby preventing the formation of sulphocyanate of potassium, and is itself converted into sulphide of iron, which is easily transformed into ferrocyanide by the action of the aqueous cyanide. The iron is usually added in the form of filings, turnings, or smithy scales (black oxide), sometimes also in the form of spathic iron (native ferrous carbonate).

For calcining the mixture, pear-shaped iron pots were originally, and are still frequently, used; they are built into the furnace in a slanting direction, and in such a manner that the flame can play all round them. The contents are stirred with a flat iron bar, or scoop, introduced through an aperture in the lid.\*

A more complete arrangement, now adopted in the larger English works, consists of a set of iron melting pots of nearly hemispherical shape, set in brickwork, and each heated by a separate fire and circular flue. The pots are closed by iron lids having apertures for introducing the animal matters, the aperture being immediately closed by a slide after each addition. Through the lid of each pot there passes a vertical spindle, carrying a set of blades or arms for mixing the materials, and set in motion by a driving shaft worked by steam power. The pots being completely closed during the melting, the atmosphere within them is maintained in a deoxidising condition, and thus the formation of cyanates is prevented.†

As iron pots heated from below cannot be raised to the high temperature which is most favourable to the success of the process without subjecting them to very rapid wear, the calcination is frequently performed, especially in Germany, in a reverberatory furnace, on the hearth of which is placed a cast-iron pan 4 or 5 feet wide, 4 or 5 inches deep, and several inches thick on the sides and bottom. The interior dimensions of the furnace should not be larger than is necessary for convenient manipulation, and the arch should be very flat. The mass in the pan is stirred by a thick iron bar, or crook, suspended by a chain and passing through an aperture in the side of the furnace; with this arrangement, the stirring is much more easily performed than with the old-fashioned pots. The furnaces are so arranged that when the potash has once been brought into the fused state, the doors of the fire-place may be closed, and no fresh firing is required during the introduction of the animal matters: this prevents the access of air to the melting mass which would oxidise it, and lead to the formation of cyanate of potassium, which would entail loss of cyanogen. Ordinary reverberatory furnaces with fire-brick hearths cannot be used for the fusion, because the hearth would be strongly attacked by the melting potash, and a large quantity of silicate of potassium would be formed.

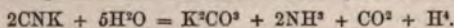
The fuel used is either wood or coal. When the process is performed in a rever-

\* A figure of the arrangement is given in the new edition of *Ure's Dictionary of Arts, Manufactures, and Mines*, vol. III. p. 480.

† For a figure and full description of this arrangement, see *Knapp's Chemical Technology*, edited by Richardson and Watts, vol. I. part 4.



beratory furnace the fuel should be very dry; for if aqueous vapour comes in contact with the heated mass, a considerable quantity of the cyanide will be decomposed, yielding carbonate of potassium, ammonia, carbonic anhydride, and free hydrogen:



Quite recently the use of gas-generators with a blast of air has been introduced into the manufacture of ferrocyanide of potassium; it presents many advantages, in particular that of facilitating the regulation of the temperature and the admission of oxygen, so as to produce at pleasure either, an ordinary, a neutral, or a reducing flame. According to Hoffmann, it is advisable, at the beginning of the process, to burn the flame-gases completely by the admission of a sufficient quantity of oxygen, so as to produce a very high temperature, which materially facilitates and expedites the process, at the same time that the excess of carbon in the animal matters, and the combustible gas evolved from the melting mass, prevents the oxygen from coming in contact with the metal, and thereby converting the cyanide of potassium into cyanate.

The melting process is conducted as follows. The pearl-ash (2 to 5 cwt. according to the dimensions of the furnace), or a mixture of 1 pt. pearl-ash and 2 to 4 pts. *blue salt* or *blue potash* obtained in a preceding operation (*vid. inf.*), is melted in the iron vessel (which takes about two hours), and heated to bright redness, so that the mass may not be too much cooled by the introduction of the animal matters. These, or an equivalent quantity of animal coal mixed with 6 to 8 per cent. iron, are then added in successive portions, first at shorter, afterwards at longer intervals. For every 100 pts. of pearl-ash, from 100 to 125 parts of fresh animal substances are taken, often a mixture of several kinds of animal matter containing different proportions of nitrogen, horn and rags for example. Sometimes a smaller quantity of uncharred animal matter is taken, and the amount made up with animal coal; the latter is seldom used alone. Each addition of animal matter causes a violent reaction and evolution of combustible gases, viz. carbonic oxide and hydrocarbons, together with water and carbonic acid, and the mass becomes thickened, less by the admixture of solid matter than by the fall of temperature resulting from the abundant formation of gas; active stirring must therefore be resorted to, in order to mix the materials well together and accelerate the decomposition. After a while, the mass gradually becomes hotter and more fluid, and carbonic oxide is evolved in consequence of the reduction of potassium. After this reaction has gone on for  $1\frac{1}{2}$  to 2 hours more, the decomposition is complete. The pasty mass is then ladled out into small cast iron dishes of about 2 inches diameter, and the furnace is again heated and filled with potash. In this manner, from 4 to 6 melting operations may be performed in 24 hours. The higher the temperature of the furnace, up to a certain point, the more quickly does the reaction take place, and the more abundant generally speaking is the product. If the heat is too low, the reduction of the potassium does not take place fast enough; and if it is too high, the cyanide and other potassium-salts volatilise and condense in the flues. A loss of product may arise from the decomposing action of aqueous vapour evolved from the animal matters: hence, according to Habich, it is best to dry these substances previously by means of over-heated steam, continuing the action till a slight evolution of ammonia begins, and substances like horn and rags are rendered friable.

*b. Lixiviation.*—The metal, which in a well conducted process, should yield about 16 per cent. of ferrocyanide, is broken into lumps when cold, and thrown into large iron pans filled with cold water, mixed with the weak lyes of former operations. The liquid is then heated to  $80^\circ$  or  $90^\circ$  C. ( $176^\circ$  to  $194^\circ$  F.), and constantly stirred to dissolve the metal as quickly as possible, because a portion of the cyanide of potassium is decomposed during the lixiviation into ammonia and formate of potassium (p. 198), and the amount thus lost increases as the operation is protracted. According to Brunnequell, the metal should be macerated for 24 hours in water of  $50^\circ$  to  $60^\circ$  C. ( $122^\circ$  to  $140^\circ$  F.), and then boiled, in which case no decomposition takes place. According to Hoffmann, the ammonia evolved is not actually formed during the lixiviation but is previously enclosed within the pores of the metal, and, dissolving in the cold water, is evolved when the liquid is heated.

As soon as the lye has attained a density of 1.16 to 1.22 ( $20^\circ$  to  $26^\circ$  Baumé), it is left to clarify without further heating; the clear solution is decanted from the insoluble residue, and transferred to the evaporating pans, which are usually heated by the waste heat of the melting furnaces. It is then brought to a density of 1.27 ( $32^\circ$  Baumé), and run off into the crystallising vessels, where it deposits a crude salt, containing, according to Hoffmann, about  $\frac{1}{4}$  of pure ferrocyanide of potassium.

*c. Crystallisation.*—The crude salt obtained as above mentioned is dissolved in warm water, so as to form a solution of specific gravity 1.27 ( $32^\circ$  Baumé), and this solution, after clarification, is transferred to the crystallising vessels. These are sometimes made of wood, but the salt crystallised in such vessels generally has a green



colour arising from a decomposition, produced, according to Gentele, by the tannin of the wood. On this account, cast-iron crystallisers are more generally preferred. The liquor is left to crystallise slowly, the crystallisation often going on for weeks in large vessels; the mother-liquor is drawn off, and if not too impure, is used to dissolve fresh quantities of crude salt; after being used two or three times for this purpose, it serves for the preparation of *blue-salt*.

The ferrocyanide is deposited in crusts in the crystallising vessels; but by suspending lumps of the solid salt in the solution by threads, it may be obtained in long bunches of crystals (*Krystalltrauben*), and by suspending these in fresh lyes, they may be obtained of great size. The salt thus obtained may be further purified by recrystallisation; 100 pts. of crude salt yield about 90 pts., or if pure materials have been used, 97 pts. of pure ferrocyanide of potassium.

The *green salt* above mentioned may be purified by recrystallisation, with addition of a small quantity of an oxidising agent, such as arsenious acid, or better, of ferricyanide of potassium (red prussiate). According to Hoffmann, the green colouring sometimes arises from the presence of sulphide of iron and potassium.

Commercial yellow prussiate often contains sulphate of potassium, which indeed may be present in considerable quantity without altering the appearance of the salt. This impurity is not easily removed by recrystallisation. The best mode of purification is to decompose the sulphate with chloride or acetate of barium, separate the resulting chloride or acetate of potassium by repeatedly crystallising the filtered solution, or by precipitating it with alcohol, then wash the precipitate with alcohol, and recrystallise from water. On the large scale, the sulphate may be completely separated by evaporating the solution to specific gravity 1.31 (35° Bm.), whereupon the greater part of the sulphate crystallises out, then drawing off the clear liquor, diluting it to specific gravity 1.28 (30° Bm.), and leaving it to cool: it then deposits pure ferrocyanide of potassium. A further portion may be obtained in like manner from the mother-liquors. For technical use, however, the sulphate of potassium is not directly injurious, but merely objectionable in so far as its presence diminishes the proportion of ferrocyanide.

*Treatment of the residues.*—The mother-liquor of the crude salt concentrated to a density of 1.33 to 1.38 (30° to 40° Bm.) deposits, on standing, nearly all the remaining ferrocyanide in the form of a fine-grained powder. The last mother-liquor contains a considerable quantity of carbonate of potassium, together with hydrate, chloride, sulphocyanate and silicate of potassium. When concentrated to a specific gravity of 1.45 (45° Bm.), it deposits the greater part of the silicate, chloride, &c., of potassium, and the mother-liquor still remaining, which contains the greater part of the carbonate, is evaporated to dryness and calcined in reverberatory furnaces provided with iron pans like the melting furnaces. The dry residue, called *blue-salt*, or *blue-potash* (*Blausalz*, or *Blaukali*), which contains from 70 to 80 per cent. of carbonate of potassium, is used, instead of potashes, or mixed with it, in subsequent melting operations.

According to analyses by Brunnequell (1), and Hoffmann (2, 3, 4 and 5), slightly calcined blue salt contains in 100 pts.:

	1.	2.	3.	4.	5.
Carbonate of potassium . . . . .	71.9	71.0	82.4	75.1	44.1
Silicate . . . . .	11.9	9.5	7.6	8.8	22.8
Sulphide . . . . .	4.3	1.4	3.8	8.3	8.7
Chloride, sulphocyanate, phosphate and } sulphate of potassium . . . . .	8.2	13.0	7.1	10.1	26.7
Insoluble matter . . . . .	1.6				
Water and loss . . . . .	2.1				

Analysis 1 is from a melting with crude potash of 75 per cent.; 2 is blue salt from a melting conducted in the ordinary way with pearl-ash; 3, with pearl-ash of better quality; 4, from a melting made with blue salt; 5, with impure potash. The last three analyses show clearly the rapid increase of the impurity of the blue-salt when impure materials are used, and the necessity of purifying it; since, when the proportion of silica increases, part of the potash is rendered insoluble and remains in the deposit, being thus lost to the process.

The *insoluble residue* or *deposit* which remains in the lixiviation of the metal, varies in quantity and composition according to the nature and proportions of the animal matters and the alkali used in the preparation; it also contains matter carried over from the fuel. Karmrodt obtained from 100 pts. of metal the following quantities of ash, each being the mean of 10 analyses:

	Rags	Horn	Hair	Leather	Charcoal (bad)
By the use of . . . . .					
Insoluble salt . . . . .	28.3	1.8	23.0	35.1	38.7

The composition of three samples of insoluble residue is shown in the following table:

Potash ( $K_2O$ ) . . . . .	12.2	16.7	10.2
Lime . . . . .	16.2	18.4	19.6
Magnesia . . . . .	2.1	1.3	1.0
Alumina . . . . .	4.8	10.2	14.2
Iron, with sesquioxide . . . . .	16.1	2.1	3.1
Manganese . . . . .	0.4	0.06	0.7
Copper . . . . .	trace	0.4	0.02
Silica . . . . .	21.1	29.7	26.4
Sulphuric acid ( $SO_3$ ) . . . . .	1.2	0.2	1.8
Phosphoric acid ( $P_2O_5$ ) . . . . .	10.4	6.4	4.9
Charcoal . . . . .	6.1	4.2	9.2
Sulphur, chlorine, cyanogen, and loss . . . . .	9.4	10.34	8.88
	100.0	100.00	100.00

The following analyses of insoluble residues from the prussiate of potash manufacture, are by Dr. Richardson of Newcastle.

	Fresh residue.	Old residue.
Sulphate of potassium with traces of sulphate of calcium, and of the chlorides of sodium and magnesium . . . . .	9.06	3.21
Phosphates of calcium, magnesium, and iron . . . . .	13.74	6.24
Sesquioxide of iron . . . . .	13.34	19.58
Lime and Magnesia . . . . .	5.08	7.23
Sand and Silica . . . . .	23.97	29.24
Charcoal and Moisture . . . . .	34.81	34.50
	100.00	100.00

The sample of old refuse was taken from a heap near the manufactory, which had lain exposed for a long time to the weather.

Hoffmann found in 100 pts. of dried residue which had been thoroughly lixiviated with cold water, from 20 to 30 pts. of silica in combination with alkali, which, if calculated as carbonate of potassium, amounted to between 20 and 30 pts. A considerable quantity of this alkali appears to be soda, and as the whole of the soda contained in the pearl-ash passes into this insoluble residue, Hoffmann suggests that a quantity of soda equivalent to the potash found in the residue might be added in the melting without diminishing the amount of ferrocyanide of potassium obtained.

The large amount of potash in the insoluble residue, together with the phosphoric acid and the decomposable silicates, renders it well adapted for the preparation of artificial manures. It may also be used for the manufacture of alum by moistening and heating it with strong sulphuric acid, and adding sulphate of alumina. Or, again, the alkali may be extracted from it as carbonate by igniting it with an equal weight of carbonate of lime and lixiviating (Karmrodts); according to Hoffmann, however, this treatment does not extract from the residue a larger amount of alkaline carbonate than simple calcination and lixiviation, or boiling with milk of lime, by which he finds that two-thirds of the whole amount of potash may be extracted. Hoffmann is of opinion that the whole of the potash might be thus extracted from the residues in the soluble form, if they could first be freed from silica. Whether it is more profitable to extract the potash from these residues and use it in subsequent operations, or to apply the residues to the preparation of manure, must depend on local circumstances.

The manufacture of ferrocyanide of potassium is still very imperfect in an economical point of view. Besides the loss of potash in the insoluble residue, there is a very large loss of nitrogen, first, because the greater portion of that element contained in the animal matter used is not converted into cyanogen at all, and secondly, because part of the cyanide of potassium in the metal is lost by decomposition, and another portion remains in the mother-liquor, so that out of 100 parts of ferrocyanide, which ought to be obtained from the metal, about  $\frac{1}{15}$  is lost when pure materials are used, and about  $\frac{1}{2}$  when the materials are impure.

During the year 1847, a series of experiments was undertaken by Messrs. Lee and Richardson\*, to ascertain how far it was possible to prevent the loss of nitrogen in the present mode of manufacturing prussiate of potash.

The experiments were on a large laboratory scale, and the fusions were conducted in

\* Communicated by Dr. Richardson.

gun-barrels. Several preliminary experiments were made with the ordinary mixture in the usual method, to enable the authors to acquire a familiarity with the nature and character of the operations.

In the subsequent experiments the same mixture of materials was always employed.

Pure horn, carefully and finely rasped, was mixed with pure potashes and clean iron filings. A small quantity of water was added to assist in making an intimate mixture, which was carefully and thoroughly dried and then reduced to a fine powder. This mixture was composed of:

Horn . . . . .	16.00
Potashes . . . . .	17.72
Iron . . . . .	3.00
Moisture . . . . .	3.28—40 oz.

The potash-charcoal was made by soaking 13 oz. of wood-charcoal with a solution of 4 oz. of potashes, and then carefully dried.

The gun-barrel was partially filled with the first mixture and exposed to a red heat in a distinct furnace. In the first and second series of experiments, the gases generated in the retort were passed through the potash-charcoal, which was kept at a red heat in another iron tube in connection with the retort-tube. In the third series of experiments, the gases were passed through hydrochloric acid. In the fourth series, the gases were passed through the red-hot potash-charcoal, and afterwards successively through hydrochloric acid and a solution of potash. In the last series, the gases escaping were collected and analysed.

In each case the prussiate was carefully extracted and crystallised. The ammonia was estimated in the usual manner, and in the tabulated results which follow, the equivalent of this ammonia is calculated in crystallised prussiate of potash.

The theoretical yield of prussiate was 382.50 and the actual quantities obtained and calculated were as follows, from the

	1.	2.	3.	4.
Retort . . . . .	101.97	135.46	146.93	141.08
Tube . . . . .	68.25	63.54		71.00
Acid . . . . .			140.24	58.80
Potash . . . . .				2.75
Total . . . . .	170.22	199.00	287.17	273.63
Loss . . . . .	212.28	183.50	95.33	108.87
	<u>382.50</u>	<u>382.50</u>	<u>382.50</u>	<u>382.50</u>
Produce per cent. . . . .	44.5	52.2	76.1	71.5

The gas evolved from the fourth experiment was collected after all the air had been expelled from the apparatus, and consisted of:

Hydrogen . . . . .	46.00
Carburetted hydrogen . . . . .	14.66
Carbonic oxide . . . . .	25.34
Nitrogen . . . . .	14.00
	<u>100.00</u>

Hence it appears that a considerable portion of the nitrogen of the organic matter is lost in a form which cannot be recovered in any shape available for manufacture of a commercial article.

From experiments on the proportion of the nitrogen of animal matter which is actually rendered available in the production of yellow prussiate, Karmrodt has obtained the results given in the following table:

<i>Animal substances used.</i>	<i>Proportion of Nitrogen converted into Cyanogen.</i>
Woollen rags . . . . .	1/6
Horn . . . . .	1/6
Leather-cuttings . . . . .	1/3
Cow-hair . . . . .	1/7
Horn-charcoal (50 pts. charcoal from 100 pts. horn) . . . . .	4/7
Rag-charcoal (75 pts. charcoal from 100 pts. rags) . . . . .	1/3

From the analysis of well-fused "metal" from a factory of yellow prussiate, Karmrodt obtained the following results:



Substance used.	Nitrogen converted into Cyanogen.
Dried blood . . . . .	1/6
Leather-cuttings . . . . .	1/5
Horn . . . . .	1/8
Woollen rags . . . . .	1/9

The greater part of the nitrogen thus lost to the process goes off in the form of ammoniacal salts; the quantity of these salts increasing as the temperature of the mass becomes lower: hence a too rapid addition of the animal matters diminishes the quantity of cyanide obtained; on the other hand, the product is increased by keeping the melted mass at a very high temperature.

Numerous attempts have been made to render available the ammonia given off in the process. With this view the animal substances were formerly subjected to dry distillation, in the first instance, to obtain ammoniacal salts, and only the residual azotised charcoal was used for the preparation of yellow prussiate. Now, however, that ammoniacal salts can be obtained so cheaply from other sources, as from the ammoniacal liquor of the gas-works, in England, and from sewage water in Paris, this mode of saving the nitrogen can scarcely be made to pay; and, according to the general experience of manufacturers, the amount of cyanide obtained is not so great when the animal matters have been previously distilled, as when they are used in their original state.

Another mode of utilising the ammonia evolved in the process, is to pass it over an ignited mixture of charcoal or coke and potash, and thus convert it into cyanogen (see page 198). There can be no doubt of the possibility of producing cyanogen in this manner, and several patents have been taken out for performing it on the large scale\*, but it does not appear that any of them have yet been profitably worked. Brunnquell suggests to pass the gases evolved by the dry distillation of animal substances through a red-hot tube of fire-clay filled with lumps of charcoal about the size of a nut, in order to convert the ammonia into cyanide of ammonium, pass the vapour of this salt, together with undecomposed carbonate of ammonium, into a moderately dilute solution of protosulphate of iron,—and boil the resulting precipitate, containing protocyanide of iron, with carbonate of potassium, to convert it into yellow prussiate. This process would certainly have the advantage of avoiding the contamination of the product with silica and the ash of the animal substances.

Another source of loss in the ordinary process is that a certain portion (from  $\frac{1}{10}$  to  $\frac{1}{5}$ ) of the cyanide of potassium in the crude lye obtained by lixiviating the metal, is not converted into ferrocyanide, even by prolonged digestion with sulphide or oxide of iron. The best mode of proceeding, according to Hoffmann, is to draw off the first liquor into a large cistern containing a considerable quantity of carbonate of iron: the cyanide of potassium will then be completely converted into ferrocyanide in the course of twenty-four hours.

If the metal contains much sulphur and not enough iron to take up the whole of it, a portion of the cyanide of potassium will be converted into sulphocyanate during the lixiviation of the metal with warm water. Hoffmann finds that the sulphocyanate is easily desulphurised by metallic iron on the small scale, but not in the manufacturing process. Scale-oxide of iron added to the metal at the end of the melting process, easily decomposes the sulphocyanate, but forms cyanate of potassium instead of cyanide. Habich desulphurises the solution with native carbonate of iron, previously freed from the carbonates of lime and magnesia by digestion with sesquichloride of iron. The complete conversion of the sulphocyanate into cyanide, would increase the quantity of yellow prussiate obtained from a given quantity of raw material from 100 to 116 pts.

As animal matters are very valuable for the preparation of manures, various attempts have been made to obtain the nitrogen required for the production of ferrocyanides from other and cheaper sources, especially from the air. That cyanides can be formed by passing atmospheric nitrogen over carbon impregnated with potash, has been satisfactorily proved by several experiments, especially by those of Fownes and of Bunsen (p. 198); and it has also been found possible to carry out this mode of formation on the manufacturing scale. Possoz and Boissière first established a manufactory for this purpose at Grenelle near Paris, in 1845, but afterwards transferred their operations to Newcastle, where fuel could be obtained at a much smaller cost. Their process, improved by Mr. Bramwell of Newcastle, consisted in passing a current of air over charcoal powder saturated with carbonate of potassium, and heated to whiteness for ten hours in wide earthen cylinders placed in an upright position.† The charcoal was

\* For a description of Berry's process (patented) see *Ure's Dictionary of Arts, Manufactures, and Mines*, vol. iii.

† For a description and drawing of the apparatus, see *London Journal of Arts*, 1845, p. 380; *Reperatory of Patent Inventions*, 1847, p. 280; also *Graham's Elements of Chemistry*, 2nd ed. vol. i. p. 387.

afterwards mixed with pulverised native carbonate of iron and lixiviated. The factory was in operation for two years, during which it produced 1000 kilogrammes (about a ton) of yellow prussiate daily. It was, however, not found to work profitably, and was ultimately abandoned, chiefly, it appears, on account of the large expenditure of fuel, and because the cylinders, whether of fire-clay or iron, were unable to withstand the intense heat to which they were exposed.

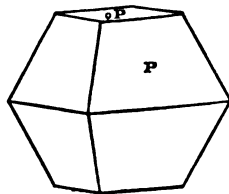
Mr. Spencer, of the Commercial Road, London, patented a process in 1837, for making use of the waste lime and lime-liquor of gas-works for the preparation of yellow prussiate and prussian blue. This gas-lime certainly contains cyanides, but the proportion appears to be too small to yield a profitable result.

The alteration which appears to present the greatest hope of improvement in the manufacture of ferrocyanide is the substitution of baryta for potash. Margueritte and De Sourdeval have shown that cyanide of barium is easily formed by passing a current of air over an intimate mixture of charcoal and baryta at a bright red heat. The baryta, not being fusible, forms with the charcoal a porous mass which the nitrogen can easily penetrate, and thus an immense number of points of contact between the carbon and nitrogen are at once obtained, whereas carbonate of potassium fuses, and the nitrogen can act only on its surface. Equally favourable results are said to have been obtained by passing the ammoniacal vapours obtained by the distillation of animal substances over a mixture of charcoal and baryta.

Another process, recently introduced by G élis (Rép. Chim. app. 1862, p. 370), consists in forming sulphocyanate of potassium by distilling a mixture of disulphide of carbon and sulphhydrate of ammonium with sulphide of potassium, and converting the sulphocyanate into yellow prussiate by heating it to dull redness with metallic iron. (See SULPHOCYANATES.)

*Properties of Ferrocyanide of Potassium.*—The pure salt crystallises with 3 at. water,  $K^+Fe^+Cy^+ + 3H^+O$ , in truncated pyramids belonging to the dimetric or quadric system. Ordinary form P. oP (like fig. 362), sometimes also with Poo and ooPoo. The crystals are often reduced to the tabular form by predominance of the face oP. Length of principal axis = 1.768. Inclination of P : P in the terminal edges =  $97^\circ 56'$ ; in the lateral edges =  $136^\circ 24'$ . They are generally lemon-yellow, turbid, or translucent, sometimes amber-yellow, or orange-yellow and quite transparent; transparent crystals appear to be formed especially by the cooling of large masses of the solution. The crystallised salt has a specific gravity of 1.83. It is permanent in the air at ordinary temperatures. The water of crystallisation begins to escape at  $60^\circ C.$  ( $140^\circ F.$ ), but is not given off completely even at  $100^\circ C.$ , unless the salt is reduced to powder and stirred for some time in contact with the air. The anhydrous salt is a white powder. The crystals contain exactly so much water (12.77 per cent. = 3 at.) that they may be regarded as *anhydrous hydrocyanate of ferrous oxide and potash* ( $K^+Fe^+Cy^+ + 3H^+O = 2K^+O.Fe^+O.6HCy^+$ ). Ferrocyanide of potassium is inodorous, has a sweetish, saline, rather bitter taste, a neutral reaction, and is not poisonous.

Fig. 362.



The crystallised salt dissolves in 2 pts. boiling and 4 pts. cold water, forming a pale yellow solution. According to Michel and Kraft (Ann. Ch. Phys. [3] xli. 471), a litre of the solution saturated at  $15^\circ C.$  (which has a specific gravity of 1.144) contains 258.77 grms. salt, and 885.34 grms. water. The salt is insoluble in alcohol, and is precipitated by alcohol from its aqueous solution in yellowish-white pearly scales.

*Decompositions.*—1. Ferrocyanide of potassium heated in a close vessel melts at little above a red heat, giving off nitrogen and leaving a mixture of cyanide of potassium and carbide of iron. If, however, it contains moisture, it likewise evolves carbonic acid, ammonia, and prussic acid. When the salt is heated with a sufficient quantity of hydrate or carbonate of potassium, no nitrogen is evolved, but the residue contains the whole of the cyanogen in the form of cyanide and cyanate of potassium, mixed with metallic iron, which sinks to the bottom of the melted mass. On this reaction is founded the preparation of the impure salt called "Liebig's cyanide of potassium," which is largely employed for galvanic gilding.

2. Both the crystals and the solution decompose slowly when exposed to light, giving off hydrocyanic acid, depositing ferric oxide or prussian blue, and acquiring an alkaline reaction. The solution is also slowly decomposed by boiling in an open vessel, ammonia being given off and the liquid becoming alkaline.

3. Oxygen, in its ordinary state, does not alter ferrocyanide of potassium at ordinary temperatures; but in an atmosphere containing ozone, as for example in a bottle containing moist phosphorus, the salt is gradually converted, from without inwards, into

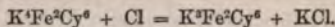


ferrieyanide (red prussiate). The same transformation takes place when a solution of the salt is subjected to the action of the *electric current*, ferrieyanide of potassium being formed at the positive pole, while hydrogen and potash are eliminated at the negative pole.

4. The salt *heated to redness in contact with the air* is converted into cyanate of potassium; also when ignited with reducible *metallic oxides*, such as the oxides of lead and iron, peroxide of manganese, &c. In fact, fused ferrocyanide of potassium reacts with oxides and sulphides just like the cyanide, inasmuch as it is converted into cyanide by fusion.

5. The aqueous solution is converted by finely divided *peroxide of lead* into ferrieyanide of potassium, slowly in the cold, more quickly when heated, completely in a few hours at the boiling heat: the other products of the reaction are carbonate of potassium and basic carbonate of lead. The same transformation is produced, though less easily, by finely divided *peroxide of manganese*; on the addition of a dilute acid, it takes place quickly. *Permanganate of potassium* converts ferrocyanide of potassium chiefly into ferrieyanide, together with a small quantity of nitrate.

6. *Chlorine* converts either the pulverised salt or the solution into ferrieyanide of potassium:



*Bromine* acts in a similar manner. (Smee.)

7. *Iodine* dissolves abundantly in a warm solution of ferrocyanide of potassium, if only a sufficient quantity is added to form an olive-green solution. An iodo-ferrieyanide of potassium,  $\text{KI.K}^{\text{f}}\text{Fe}^{\text{c}}\text{Cy}^{\text{e}}$ , is deposited on cooling, in the form of a golden-yellow crystalline powder having a silky lustre. (Preuss, Ann. Ch. Pharm. xxix. 323.)

8. Strong *nitric acid* heated with ferrocyanide of potassium decomposes it completely, giving off cyanogen, nitrogen, nitric oxide, and carbonic acid, and forming ferric oxide and nitrate of potassium. Moderately strong nitric acid dissolves it, forming a coffee-coloured solution, which contains nitro-ferrieyanide or nitro-prusside of potassium (p. 250).

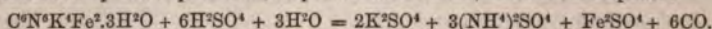
9. Aqueous *chloric and iodic acids* are said to convert the ferrocyanide into ferrieyanide, with evolution of chlorine or iodine.

10. *Chromic acid* and soluble chromates convert the ferrocyanide into ferrieyanide. (Schönbein, J. pr. Chem. xx. 145.)

11. The ferrocyanide melted with *sulphur* is converted into sulphocyanate of potassium, mixed, according to the temperature, with protocyanide of iron, sulphocyanate of iron or mellone-compounds. (See SULPHOCYANATES.)

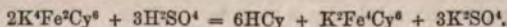
12. Fused in like manner with *selenium*, it yields selenocyanate of potassium (g. v.)

13. Heated with *strong sulphuric acid*, it gives off carbonic oxide, and leaves a residue of sulphate of potassium, sulphate of ammonium, and ferrous sulphate:



When the acid is first poured on the pulverised salt, the mass becomes hot and gives off a small quantity of prussic acid. On applying heat, the white pasty mass dissolves and gives off abundance of carbonic oxide, which is pure, excepting that it has a slight garlic odour; no hydrocyanic acid passes over with it, but only a trace of formic acid; finally also a small quantity of sulphurous anhydride is evolved; but if the heat be continued after all the carbonic oxide has passed over, large quantities of sulphurous anhydride are evolved and the ferrous sulphate is converted into ferric sulphate, which unites with the sulphate of potassium, forming an iron-alum,  $\text{K}(\text{Fe}^{\text{f}})^{\text{f}}2\text{SO}^{\text{a}}$ . (Fownes, Phil. Mag. [3] xxiv. 21; see also Grimm and Ramdohr, Ann. Ch. Pharm. xeviii. 127.)

14. The *stronger acids* added in the state of *dilute solution*, and not in too great excess, to a solution of ferrocyanide of potassium, produce no apparent alteration; but subsequent treatment with ether shows that ferroprussic acid has been separated (p. 226). The mixture becomes turbid when heated; boils below  $100^{\circ}\text{C}.$ ; gives off half the cyanogen of the ferrocyanide in the form of hydrocyanic acid; deposits the white or yellow powder of ferrocyanide of iron and potassium,  $\text{K}^{\text{f}}\text{Fe}^{\text{c}}\text{Cy}^{\text{e}}$ ; and then contains in solution a compound of the acting acid with three-fourths of the potassium. Supposing that the ferrocyanide of potassium is not completely decomposed in the cold—which, though not certain, may be assumed as true when only 3 at. sulphuric acid are used—the equation will be:



But, if the ferrocyanide of potassium is completely decomposed at the commencement, without the aid of heat, into ferroprussic acid and a potassium-salt, we must suppose

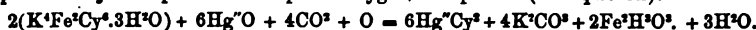


that the ferroproussic acid, when resolved by heat into hydrocyanic acid and  $\text{H}^+\text{Fe}^+\text{Cy}^-$  again takes up 2 at. potassium from the potassium-salt produced:

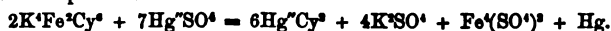


According to calculation, 211.4 parts (1 at.) of crystallised ferrocyanide of potassium, yield 40.6 pts. ( $1\frac{1}{2}$  at.) or 19 per cent. of hydrocyanic acid.

15. Ferrocyanide of potassium boiled with *mercuric oxide* is gradually decomposed, with formation of mercuric cyanide, which remains in solution, together with carbonate of potassium formed by absorption of carbonic acid from the air, while ferric hydrate produced by absorption of atmospheric oxygen, is deposited (Vauquelin):



If the quantity of mercuric oxide is not sufficient for complete decomposition, the liquid deposits pale yellow rhombic tablets, probably a double salt of cyanide of mercury with ferrocyanide of potassium (Preuss, Ann. Ch. Pharm. xxix. 324). When 1 pt. ferrocyanide of potassium is boiled with 2.5 pts. *mercuric sulphate* and 8 pts. water, cyanide of mercury is formed, together with sulphate of potassium and ferric sulphate, and metallic mercury is precipitated, together with a small quantity of a greenish-white powder:



The ferrocyanide boiled with *mercuric nitrate* or *chloride*, forms a double salt,  $\text{K}^+\text{Hg}^+\text{Cy}^- + 2\text{aq.}$ , which crystallises in white micaceous laminae (Desfosses). The hot solution of the ferrocyanide takes up a large quantity of *mercuric iodide*, and on cooling deposits a double salt which crystallises in laminae. (Preuss.)

16. When the solution of the ferrocyanide is boiled with *nitrate of silver*, a dirty blue precipitate of ferrous cyanide is produced, while cyanide of silver and potassium remains in solution:



A similar reaction takes place with chloride of silver (Gerh. i. 327):



17. When the solution of ferrocyanide of potassium is boiled with a few drops of *aquichloride of iron*, a certain quantity of ferricyanide of potassium is formed, so that the liquid yields a deep blue precipitate with ferrous salts:



A small quantity of ferricyanide is also formed on boiling the ferrocyanide with a large excess of prussian blue. (Williamson, Ann. Ch. Pharm. lvii. 238.)

18. When ferrocyanide of potassium is heated with *sal-ammoniac*, either dry or in solution, cyanide of ammonium volatilises, while chloride of potassium and chloride of iron remain (Duflos, Schw. J. lxx. 106. Bineau, Ann. Ch. Phys. lxxvii. 231.)

19. The aqueous solution of ferrocyanide of potassium forms with the salts of most of the *earth-metals* and *heavy-metals*, precipitates consisting of ferrocyanides of those metals, e.g.:



the precipitate generally carries down with it a small quantity of the alkaline ferrocyanide, which is difficult to remove by washing. The colours of many of those precipitates are very characteristic, and render ferrocyanide of potassium a valuable reagent for the detection of metals in solution. The colours exhibited by the most important metals are given in the following table.

#### Reactions of Ferrocyanide of Potassium with Metallic Solutions.

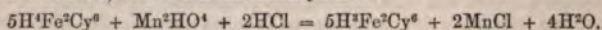
Salts of Aluminium . . .	White precipitate (after some time only).
" Antimony . . .	White.
" Bismuth . . .	White, insoluble in hydrochloric acid.
" Cadmium . . .	White, soluble in hydrochloric acid.
" Chromium . . .	No precipitate.
" Cobalt . . .	Yellowish-green, turning grey after a while; insoluble in hydrochloric acid.
" Copper (cupric) . . .	Red-brown, insoluble in hydrochloric acid.
" Gold . . .	Emerald-green coloration; no precipitate.
" Iron: (ferrous) . . .	White precipitate, quickly turning blue in contact with the air; insoluble in hydrochloric acid.
(ferric) . . .	Deep-blue, insoluble in hydrochloric acid.

Salts of Lead . . .	White.
" Magnesium . . .	White (only in concentrated solutions).
" Manganese . . .	White, soluble in hydrochloric acid.
" Mercury (mercurous) . . .	White, gelatinous.
" " (mercuric) . . .	White, becoming blue after a while, from formation of prussian blue.
" Molybdenum . . .	Brown. (See page 230.)
" Nickel . . .	White, with greenish tinge, insoluble in hydrochloric acid.
" Silver . . .	White.
" Tin (stannous and stannic) . . .	White, gelatinous.
" Uranium (uranous) . . .	Light-brown.
" " (uranic) . . .	Red-brown.
" Zinc . . .	White, gelatinous, insoluble in hydrochloric acid.

The solutions to which the reagent is applied should be moderately acidulated: too great an excess of acid is likely to decompose the ferrocyanide of potassium, and thus mask the reaction; and in alkaline liquids the precipitates are not produced at all.

The presence of iron in ferrocyanide of potassium is not exhibited either by caustic alkalis, or by sulphide of ammonium.

*Estimation of Ferrocyanide of Potassium.*—The amount of this salt contained in a solution, may be determined by means of *permanganate of potassium*, which, when added to an acidulated solution of the ferrocyanide (containing therefore ferropussian acid in the free state) converts it into ferricyanide:



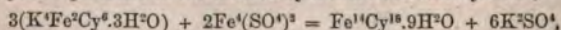
The solution of permanganate is graduated by means of a standard solution of ferrocyanide of potassium containing 20 grammes of the pure crystallised salt in a litre; of this solution 10 cub. cents. are diluted with 250 cub. cents. water; the liquid is acidulated with hydrochloric acid; and the solution of permanganate is then added till the yellow colour of the liquid changes to the yellowish-red of the ferricyanide. As the solution of permanganate changes very rapidly, this mode of graduation (which is very quickly executed) must be repeated before each series of determinations.

To apply the method to the estimation of an impure sample of yellow prussiate, 5 grammes of the salt are dissolved in 250 cc. water, and 10 cc. of the solution are treated with the solution of permanganate whose strength has just been determined. If, for example, 80 burette-divisions of the permanganate solution are required to decompose 10 cc. of the solution of pure ferrocyanide, and only 70 divisions for 10 cc. of the solution of the given sample, that sample will contain  $\frac{70}{80}$  or 87.5 per cent. of

pure crystallised ferrocyanide (De Haen, Ann. Ch. Pharm., xc. 160). Slater (Chem. Gaz, 1855, p. 460) graduates the solution of permanganate by adding it to the normal solution of ferrocyanide till the last drop no longer produces any green coloration.

This method will not, however, give accurate results, if the yellow prussiate is contaminated with any substance which can likewise exert a reducing action on the permanganate. If such are present, or suspected, the salt must be first precipitated as prussian blue (ferric ferrocyanide), and, after careful washing, reconverted into ferrocyanide of potassium by pure potash. This purified salt may then be treated by the method just described (Hoffmann).

Brunnquell estimates the amount of ferrocyanide of potassium in a sample by the quantity of a ferric salt required to precipitate a given quantity of it. The standard ferric solution is prepared by dissolving 83.70 gm. of pure crystallised ferrous sulphate in water, and boiling the solution with nitric acid till it is completely oxidised, and diluting to a litre. 100 cc. of this solution will precipitate exactly 10 gm. of pure crystallised yellow prussiate in the form of hydrated ferric ferrocyanide;



taking into account the small quantity of the yellow prussiate which is carried down with the precipitate.

To apply this solution in estimating the value of a sample of "metal" (p. 232), 10 gm. of the metal are dissolved in water; a few drops of the standard ferric solution are added from a burette, then a small quantity of dilute nitric acid, till the precipitate, which is brown at first, turns blue; the test-liquid is then added as long as prussian blue continues to form. To know when the reaction is complete, a drop of the liquid is let fall on filtering paper, and the colourless circle which forms round the blue spot is tested with ferric solution diluted for the purpose; and the addition of the iron

solution to the liquid under examination is continued till the sample on the filtering paper is turned brown on addition of the iron-salt (from formation of sulphocyanate of iron), or, till it turns blue on addition of yellow prussiate, showing that it contains a slight excess of ferric salt (Brunnquell, *Polyt. Centralb.* 1863, p. 771; *Handw. d. Chem.* 2<sup>te</sup> Aufl. ii. [2] 206).

**Ferrocyanide of Silver,  $\text{Ag}^+\text{Fe}^+\text{Cy}^-$ .**—White precipitate, turning bluish when exposed to the air; soluble in ammonia, insoluble in ammoniacal salts. When heated, it glows, gives off cyanogen and nitrogen, and leaves carbide of iron mixed with metallic silver. Nitric acid converts it into the orange-yellow ferricyanide,  $\text{Ag}^+\text{Fe}^+\text{Cy}^-$  (Glassford and Napier). Strong sulphuric acid also decomposes it, forming sulphate of silver. Other acids, even hydrochloric acid, exert no decomposing action. Cyanide of potassium converts it into argentocyanide and ferrocyanide of potassium;  $\text{Ag}^+\text{Fe}^+\text{Cy}^- + 8\text{KCy} = 4\text{KAgCy}^2 + \text{K}^+\text{Fe}^+\text{Cy}^-$ . (Glassford and Napier, *Phil. Mag.* [3] xxv. 71.)

**Ferrocyanide of Sodium,  $\text{Na}^+\text{Fe}^+\text{Cy}^- + 12 \text{H}^+\text{O}$ .**—Usually obtained by adding prussian blue to caustic soda as long as the blue colour changes to brown, then filtering and crystallising. The crystals are pale yellow, transparent, oblique rhombic prisms, efflorescing in warm air, soluble in  $4\frac{1}{2}$  pts. cold water, insoluble in alcohol.

The crystals belong to the monoclinic system. Dominant faces  $\infty\text{P}$ ,  $[\infty\text{P}\infty]$ ,  $\infty\text{P}\infty$ ,  $[\text{P}\infty]$ . Inclination of  $\infty\text{P}$ :  $\infty\text{P} = 99^\circ 40'$ ;  $\infty\text{P}$ :  $[\infty\text{P}\infty] = 139^\circ 50'$ ;  $\infty\text{P}$ :  $\infty\text{P}\infty = 130^\circ 10'$ ;  $[\text{P}\infty]$ :  $[\infty\text{P}\infty] = 127^\circ 56'$ ;  $\infty\text{P}$ :  $[\text{P}\infty] = 118^\circ 33'$ . The faces  $[\infty\text{P}\infty]$  are often much developed. (Bunsen, *Pogg. Ann.* xxxvi. 413).

As soda is very much cheaper than potash, it has been proposed to prepare ferrocyanide of sodium on the manufacturing scale by fusing carbonate of sodium with animal matter and iron. The sodium-salt is, however, much more difficult to crystallise than ferrocyanide of potassium, and would therefore be scarcely separable from the very impure lyes obtained by lixiviating the metal. The preparation of ferrocyanide of sodium, might, however, succeed by Brunnquell's process (p. 238). But, as already observed, the most promising substitute for the ordinary yellow prussiate appears to be the ferrocyanide of barium (pp. 224, 239).

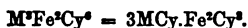
**Ferrocyanide of Sodium and Potassium,  $\text{NaK}^+\text{Fe}^+\text{Cy}^- + \frac{7}{2} \text{aq}$ .**—Obtained by treating a mixture of ferricyanide of potassium and grape-sugar with caustic soda, or by boiling a solution of the corresponding ammonium salt  $(\text{NH}_4^+)\text{K}^+\text{Fe}^+\text{Cy}^-$  with caustic soda; it may be purified by precipitating with alcohol and recrystallising. It forms rhombic or nearly square prisms, having a glassy lustre and easily soluble in water: they do not give off their water below  $200^\circ \text{C}$ . Chlorine appears to convert the salt in sodio-potassic ferricyanide,  $\text{NaK}^+\text{Fe}^+\text{Cy}^-$ . (Reindel, *J. pr. Chem.* lxx. 460.)

**FERRICYANIDES OF TIN.** } See p. 242.  
**FERRICYANIDES OF URANIUM.** }

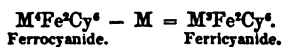
**Ferrocyanide of Zinc,  $\text{Zn}^+\text{Fe}^+\text{Cy}^- + 3 \text{aq}$ ,** is precipitated as a white powder, on mixing the solution of a zinc-salt with ferrocyanide of potassium; also, according to Jonas, by digesting metallic zinc with pulverised prussian blue mixed with hydrochloric acid; hydrogen is thus evolved, and the mixture gradually loses its blue colour, but the reaction is not complete for some days.

**Ammonio-ferrocyanide of Zinc,  $3\text{NH}_4^+\text{Zn}^+\text{Fe}^+\text{Cy}^- + \text{aq}$ ,** or **Ferrocyanide of Zinc and Diammo-zincammonium,**  $\frac{\text{NAm}^+\text{ZnH}}{\text{Zn}^+} \text{Fe}^+\text{Cy}^- + \text{aq}$ .—Obtained as a crystalline precipitate on adding ferrocyanide of potassium to a dilute solution of a zinc-salt supersaturated with ammonia. (Bunsen, *Pogg. Ann.* xxxiv. 136; Monthiers, *J. Pharm.* [3] xi. 253.)

### Ferricyanides or Ferridecyanides.



These salts, discovered by Leopold Gmelin, differ from the ferrocyanides only in containing 1 at. metal less with the same quantity of iron and cyanogen, and are consequently produced from the ferrocyanides by the action of oxidising (metal-abstracting) agents, chlorine, chromic acid, peroxides, &c.:



On the other hand, ferricyanides are converted into ferrocyanides by the action of reducing (metal-adding) agents; thus ferricyanide of potassium is converted by grape-sugar in presence of potash into ferrocyanide of potassium, and in presence of soda or



ammonia, into the double ferrocyanide of potassium and sodium or ammonium (pp. 224, 243). The conversion of a ferrocyanide into a ferricyanide is therefore precisely analogous to that of protochloride of iron into sesquichloride, the iron, as in other cases of oxidation, being altered in such a manner, that whereas in the ferrocyanides 2 at. iron are equivalent to 2 at. hydrogen, in the ferricyanides 2 at. iron are equivalent to 3 at. hydrogen.

The relations between the ferro- and ferricyanides may perhaps be most clearly seen by expressing their composition in equivalent instead of atomic formulæ:

Ferrocyanide of potassium . . . . .	$K^4Fe^2Cy^6$
Ferricyanide of potassium . . . . .	$K^3Fe^3Cy^6$
Ferrocyanide of iron and potassium . . . . .	$(K^2Fe^2)Fe^2Cy^6$
Ferricyanide of iron and potassium . . . . .	$(KFe^2)Fe^3Cy^6$

The equivalent formulæ of the simple ferricyanides, such as  $K^3Fe^3Cy^6$ , are divisible by 3 and may be reduced to  $MfeCy^2$  or  $MCy.feCy$ .

The ferricyanides may also be regarded as containing the compound radicle, *ferric*- or *ferrid*-cyanogen,  $Fe^3Cy^2 = Cfdy$ : e. g.  $K^3Fe^3Cy^6 = K^3Cfdy$ .

The ferrocyanides of the alkali-metals are easily soluble in water and crystallise well; both crystals and solutions have a fine red colour. The ferricyanides of the alkaline earth-metals are also soluble in water; most of the others are insoluble or difficultly soluble, and may be formed by precipitation.

*Reactions of soluble Ferricyanides with Metallic Salts.*

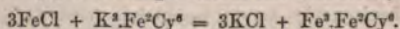
Salts of Aluminium . . . . .	No precipitate.
" Antimony . . . . .	No precipitate.
" Cadmium . . . . .	Yellow precipitate, soluble in acids, ammonia, and ammoniacal salts.
" Bismuth . . . . .	Light brown, insoluble in hydrochloric acid.
" Chromium . . . . .	No precipitate.
" Cobalt . . . . .	Dark brown-red, insoluble in hydrochloric acid.
" Copper (cupric) . . . . .	Yellowish-green, insoluble in hydrochloric acid.
" Gold . . . . .	No precipitate.
" Iron (ferrous) . . . . .	Dark blue, insoluble in acids.
" " (ferric) . . . . .	No precipitate, the liquid merely becoming a little darker.
" Lead . . . . .	No precipitate.
" Magnesium . . . . .	No precipitate.
" Manganese . . . . .	Brown precipitate, insoluble in acids.
" Mercury (mercurous) . . . . .	Red-brown, turning white after some time.
" " (mercuric) . . . . .	No precipitate.
" Nickel . . . . .	Yellowish-green, insoluble in hydrochloric acid.
" Tin (stannous) . . . . .	White, soluble in hydrochloric acid.
" " (stannic) . . . . .	No precipitate.
" Uranium (uranic) . . . . .	No precipitate.
" Zinc . . . . .	Orange precipitate, soluble in hydrochloric acid.

**FERRICYANIDE OF AMMONIUM**,  $(NH^4)^3Fe^3Cy^6 + 3 aq.$ , obtained by the action of chlorine on the ferrocyanide, forms oblique rhombic prisms, of a fine red colour, permanent in the air, very soluble in water.

**FERRICYANIDE OF COPPER**.—Yellowish-green precipitate, soluble in ammonia; and always retaining a small quantity of the alkaline ferricyanide used to precipitate it.

**FERRICYANIDE OF HYDROGEN, OR FERRIPRUSSIC ACID**,  $H^+Fe^3Cy^6 = 3HCy.Fe^3Cy^2$ , is obtained by decomposing ferricyanide of lead with an exactly equivalent quantity of dilute sulphuric acid, and evaporating the filtrate at a gentle heat. It forms brownish needles, easily decomposed by a stronger heat; reddens litmus strongly, and has a rough sourish taste. The solution gives a dark blue precipitate with ferrous salts, and alters the colour of ferric chloride to a lighter brown. (Gm. vii. 448.)

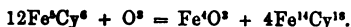
**FERRICYANIDE OF IRON**.—a. *Ferrous Ferricyanide*,  $Fe^2Cy^6 + x aq. = Fe^2Fe^3Cy^6 + x aq.$ —This compound, commonly called *Turnbull's blue*, is obtained by precipitating a ferrous salt with ferricyanide of potassium:



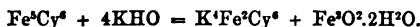
A portion of the alkaline ferrocyanide goes down with the precipitate, but may be

removed, according to Williamson, by digesting the precipitate for some time with excess of protochloride of iron, and then washing with boiling water.

Ferrous ferricyanide, when dry, is of a deep blue colour, more delicate than that of ordinary prussian blue, with a tinge of copper-red; it cannot, however, be dried completely without partial decomposition, attended with evolution of hydrocyanic acid. When heated in contact with the air, it is converted into a mixture of ferric oxide and ferric ferrocyanide (p. 227):



Heated with aqueous potash or carbonate of potassium, it is converted into ferricyanide of potassium and ferroso-ferric hydrate:

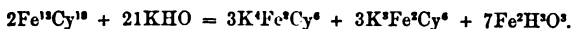


This reaction distinguishes it from ferric ferrocyanide, which yields ferric hydrate when treated with aqueous alkalis.

Turnbull's blue is occasionally used by the calico-printer, who mixes it with perchloride of tin, and prints the mixture, which is in a great measure soluble, upon Turkey-red cloth, raising the blue colour afterwards by passing the cloth through a solution of bleaching powder containing excess of lime. The chief object of that operation is indeed different, namely to discharge the red and produce white patterns where tartaric acid is printed on the cloth; but it has also the effect incidentally of precipitating the blue pigment and stannic oxide together on the cloth, by neutralising the acid of the stannic chloride. (*Graham's Elements*, 2nd edition, vol. ii. p. 40.)

b. *Ferroso-ferric Ferricyanide*,  $\text{Fe}^{\text{II}}\text{Cy}^{\text{I}} + x\text{aq.} = (\text{Fe}^{\text{II}})\text{Fe}^{\text{III}}\text{Cy}^{\text{I}} + x\text{aq.}$ —This compound, often called *Prussian green*, is produced by the action of chlorine in excess on aqueous ferro- or ferri-cyanide of potassium; also by leaving the ferrocyanide for some time in contact with aqueous acids, especially in hot solutions (Pelouze). To obtain it pure, chlorine in excess is passed into a solution of yellow or red prussiate; the liquid is heated to boiling; and the precipitate is boiled with strong hydrochloric acid to extract oxide of iron and decompose any prussian blue that may have been formed at the same time, this treatment being continued till the liquor is no longer turned blue on addition of water (Pelouze, *Ann. Ch. Phys.* [2] lxxix. 40). Williamson appears to have obtained the same compound by the action of nitric acid on ferrocyanide of iron and potassium (p. 229).

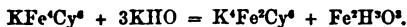
Prussian green, heated to  $180^{\circ}\text{C}$ ., gives off cyanogen, with a little hydrocyanic acid, and is converted in a short time into a violet-blue compound; by prolonged contact with the air it is converted into prussian blue. Potash decomposes it, separating ferric hydrate, and forming a solution of yellow and red prussiate:



*Potassio-ferrous Ferricyanide*,  $\text{KFe}^{\text{II}}\text{Cy}^{\text{I}} = (\text{KFe}^{\text{II}})\text{Fe}^{\text{III}}\text{Cy}^{\text{I}}$ . (Williamson *Ann. Ch. Pharm.* lvii. 228.)—This compound, which may also be regarded as *potassio-ferric ferrocyanide*,  $(\text{KFe}^{\text{II}})\text{Fe}^{\text{III}}\text{Cy}^{\text{I}}$ , is produced by the action of oxidising agents on potassio-ferrous ferrocyanide,  $(\text{K}^{\text{I}}\text{Fe}^{\text{II}})\text{Fe}^{\text{II}}\text{Cy}^{\text{I}}$  (p. 229). To prepare it, 1 pt. of the white compound is digested in a basin with 1 pt. nitric acid and 20 pts. water, the liquid being constantly stirred. As the temperature approaches the boiling-point, the compound begins to turn blue and nitric oxide is evolved; as soon as this evolution of gas becomes rapid, the basin must be removed from the fire; the gas, however, continues to escape till the solid compound has assumed a deep blue colour. If the colour be not deep enough, the compound must be again heated with fresh nitric acid, till a sample decomposed by caustic potash no longer leaves ferroso-ferric but pure ferric oxide. The product is then to be washed till the wash-water no longer leaves a residue of nitre on evaporation. If the action of the nitric acid has been too strong, the resulting blue compound, when treated with potash, yields the red instead of the yellow prussiate, and is then useless.

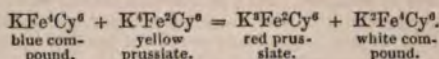
When dry, it exhibits a very beautiful violet colour, with scarcely any coppery lustre. The recently precipitated compound, suspended in water, appears green by transmitted light.

By further boiling with nitric acid, this blue compound is converted into a dark green substance, which appears to be identical with Pelouze's prussian green. It is decomposed by aqueous potash, yielding ferrocyanide of potassium and ferric hydrate:



Potassio-ferrous ferricyanide digested with solution of ferrocyanide of potassium,

converts the latter into ferricyanide, and is itself converted into white potassio-ferrous ferrocyanide :



**FERRICYANIDE OF LEAD**, obtained by mixing nitrate of lead with ferricyanide of potassium, forms dark red-brown crystals, grouped like cocks' combs: they are slightly soluble in cold water, rather more in hot water.

**FERRICYANIDE OF MAGNESIUM**.—Obtained by treating the ferrocyanide with chlorine. Very soluble, uncrystallisable.

**FERRICYANIDE OF NICKEL**.—Yellowish green precipitate, insoluble in hydrochloric acid.

On adding ferricyanide of potassium to an ammoniacal solution of nitrate of nickel, a precipitate is formed of a fine yellow colour, soluble in excess of ammonia, and having the composition of an ammonio-ferricyanide of nickel,  $2\text{NH}_4\text{Ni}^{\text{II}}\text{Fe}^{\text{II}}\text{Cy}^{\text{a}} + \frac{1}{2}\text{aq.}$ , or ferricyanide of nickel and nickel-ammonium,  $\left(\text{NH}_4\text{Ni}^{\text{II}}\right)^2\left\{\text{Fe}^{\text{II}}\text{Cy}^{\text{a}} + \frac{1}{2}\text{aq.}\right.$

**FERRICYANIDE OF POTASSIUM**,  $\text{K}^{\text{I}}\text{Fe}^{\text{II}}\text{Cy}^{\text{a}} = 3\text{KCy}^{\text{a}}\text{Fe}^{\text{II}}\text{Cy}^{\text{a}}$ . *Ferridcyanide of Potassium, Red prussiate of Potash.* (*Roth's Cyaneisenkalium, rothes Blutlaugensalz, Kaliumeisencyanid, Ferridcyanikalium.*)—This beautiful salt, which was discovered by Leopold Gmelin (Schw. J. xxxiv. 325; *Handbook*, vii. 468), is obtained by the action of oxidising agents on ferrocyanide of potassium. It is usually prepared by passing washed chlorine gas (with constant agitation, to ensure uniformity of action) through a cold solution of the yellow prussiate, till a sample tested with a ferric salt, no longer forms a dark blue precipitate, but a clear brown mixture. The liquid is then evaporated till it crystallises, and the crystals are purified by repeated crystallisation from hot water. Larger crystals are obtained by hot evaporation than by cooling from a rapidly boiled solution. The mother-liquor contains scarcely anything but chloride of potassium.

If the passage of the chlorine into the liquid is continued too long, prussian green is produced, which greatly interferes with the crystallisation, and cannot be separated by filtration, as it runs through the filters. To remove it, Posselt (*Ann. Ch. Pharm.* xlii. 170) evaporates the solution to the crystallising point, then boils it, adding a few drops of caustic potash, just sufficient to decompose the green compound and separate ferric oxide (p. 245), then filters, and leaves the solution to crystallise by slow cooling. An excess of potash must be carefully avoided, as it reconverts the red into yellow prussiate; a certain quantity of the latter is, however, necessarily formed in the decomposition of the prussian green (p. 245).

It is not, however, an easy matter to obtain perfectly pure ferrocyanide of potassium by the preceding process, partly on account of the chloride of potassium necessarily produced, partly on account of the prussian green, the formation of which can scarcely be avoided, both of these substances interfering greatly with the formation of good crystals. A sure way of obtaining a pure salt is to digest the solution of the yellow prussiate with an excess of potassio-ferrous ferricyanide (p. 245), which converts it completely into red prussiate. The liquid, filtered and evaporated, yields at once pure crystals of the red-salt. The pale blue residue on the filter, which consists of white potassio-ferrous ferrocyanide, mixed with the excess of the blue salt used, may be entirely reconverted into the latter by digestion with nitric acid, so that it may be repeatedly used for converting fresh quantities of the yellow prussiate into the red. (Williamson.)

Yellow prussiate may also be converted into red by the action of hypochlorites, by digesting the solution with finely pulverised peroxide of lead or manganese, by ozone, or by placing it in the circuit of the voltaic battery (p. 240).

For manufacturing purposes, the chlorine process is invariably used, the yellow prussiate being treated with chlorine, either in the dry or in the wet way. In the dry way, red prussiate is prepared by spreading the pulverised yellow salt on shelves in a chamber into which chlorine is passed, just as in the manufacture of bleaching powder. In this manner, a bluish-green powder is obtained, which is a mixture of the ferricyanide with chloride of potassium, likewise containing either decomposition-products of the former, or unaltered yellow prussiate.

The wet method of decomposition, which is more frequently practised, is exactly similar to the laboratory process above described. The last mother-liquors, which contain chiefly chloride of potassium with a small quantity of red (and sometimes also yellow) prussiate, are either evaporated to dryness and sold as "blue powder" for dyeing wool blue; or they are precipitated with solution of ferrous sulphate, the precipitate being sold as prussian or Turnbull's blue.

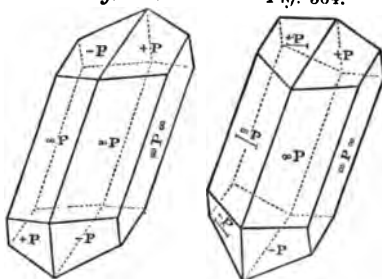
**Properties.**—Ferricyanide of potassium forms prismatic crystals of a fine blood-red



colour, sometimes very large. According to Kopp (*Krystallographie*, p. 311), they belong to the monoclinic system, the ordinary combination being  $\infty P$ .  $\infty P\infty$  . +  $P$ . -  $P$  (fig. 363). Ratio of axes  $a : b : c = 0.7457 : 1 : 0.6985$ . Inclination of  $b : c = 72^\circ 27'$ ; angle  $\infty P : \infty P$  in the clinodagonal section  $= 76^\circ 4'$ ; +  $P : + P = 105^\circ 4'$ ; -  $P : - P = 119^\circ 28'$ . Twin-crystals sometimes occur, united by the face  $\infty P\infty$  (fig. 364), and having very much the aspect of rhombic prisms. Schabus, indeed (Wien. Akad. Ber. 1850, p. 582), regards the crystals of ferricyanide of potassium as rhombic or trimetric, having their axes in the ratio 1.2418 : 1.6706 : 1, and ordinarily exhibiting the combination  $\infty P$ .  $\infty P\infty$ .  $P$ .  $\bar{P}2$ .  $\frac{3}{2}P\frac{3}{2}$ ; he attributes their monoclinic aspect to the occurrence of the face  $\bar{P}2$  in combination with  $\frac{3}{2}P\frac{3}{2}$  on the one side of the brachydiagonal principal section, and with  $\infty P$  and  $\infty P\infty$  on the other.

Fig. 363.

Fig. 364.



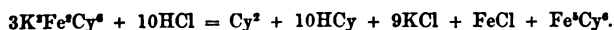
The crystals are anhydrous, and have a specific gravity of 1.800 (Schabus), 1.845 (Wallace). The salt has a saline, slightly astringent taste, neutral reaction, and yields an orange-yellow powder. It dissolves easily in water, the concentrated solution having a brownish-yellow, and the dilute solution a lemon-yellow colour.

One part of the salt dissolves :

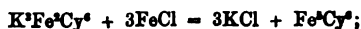
at	4.4° C.	in 3.03 pts. water,	forming a solution of specific gravity	1.151	
"	10.0	"	2.73	"	1.164
"	15.6	"	2.54	"	1.178
"	37.8	"	1.70	"	1.225
"	100.0	"	1.29	"	1.250
"	104.0	"	1.22	"	1.265

The concentrated solution boils at 104° C.; it is precipitated by alcohol, but the salt is not quite insoluble in alcohol.

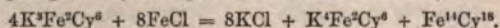
**Decompositions.**—1. The crystals heated in a close vessel decrepitate loudly, and give off cyanogen with a small quantity of nitrogen, leaving a residue containing cyanide and ferrocyanide of potassium, prussian blue, a mass resembling paracyanogen, charcoal, and iron. In the flame of a candle, the salt burns with sparks.—2. It becomes incandescent when heated with *oxide of copper*, and detonates sharply when heated with nitrate of ammonia.—3. The aqueous solution is permanent in the dark, but decomposes in *sunlight*, also when boiled for a considerable time, being converted into yellow-prussiate.—4. When the salt is *electrolysed*, yellow prussiate is formed at the negative pole.—5. *Chlorine* in excess decomposes red prussiate, chloride of cyanogen and hydrocyanic acid being evolved, whilst the liquid acquires a dark red colour, and on standing in an open vessel, or more quickly on boiling or on addition of an alkali, deposits prussian green.—6. *Bromine* acts in the same manner as chlorine (Sme e).—7. *Nitric acid* forms with the crystals, gradually, even at ordinary temperatures, a brown solution like that which it produces with the yellow ferrocyanide (p. 240); it deposits crystals of nitre, and contains nitroferrocyanide of potassium (Playfair).—8. The pulverised crystals heated with strong *sulphuric acid* become pale yellow, and impart that colour to the acid; at a higher temperature, the mass becomes bluish-white and tough; at a still higher temperature, it swells up and evolves combustible gases; and, finally, at a red heat, leaves a residue of potassio-ferric sulphate.—Sulphuric acid forms with the aqueous solution a green precipitate, which consists of  $\text{Fe}^{\text{Cy}^3}$  [?] mixed with a small quantity of cyanide of potassium, and turns blue when boiled with excess of sulphuric acid, part of the cyanogen being thereby converted into ammonia (Williamson, Ann. Ch. Pharm. lvi. 243).—9. The aqueous solution of the red salt boiled with *hydrochloric acid*, deposits ferrous ferricyanide, the reaction being probably attended with evolution of cyanogen :



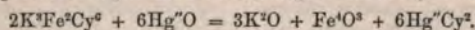
10. *Ferrous salts*, added in equivalent quantity or in excess to a solution of red prussiate, form a precipitate of ferrous ferricyanide :



but on adding to the boiling solution of the red salt, a quantity of protochloride of iron not sufficient for complete precipitation, the yellow ferrocyanide is formed, and ferric ferrocyanide is precipitated (Liebig, Ann. Ch. Pharm. lvi. 237):

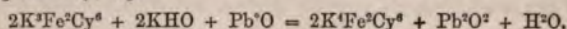


11. When the aqueous solution of ferricyanide of potassium is boiled with *mercuric oxide*, the whole of the iron is precipitated in the form of pulverulent ferric oxide, to which small quantities of potassium and cyanogen tenaciously adhere (Gmelin):

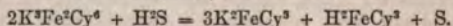


12. *Potash* does not act on the solution at ordinary temperatures, or even at higher temperatures, unless the liquid be boiled down to a high state of concentration; in that case the red prussiate is converted into the yellow prussiate and cyanide of potassium, with evolution of cyanogen (not of oxygen) and precipitation of ferric oxide (Boudault).

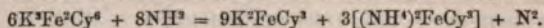
13. Many *heavy metallic oxides*, in presence of potash, convert the dissolved red prussiate into the yellow prussiate, the red salt taking up potassium, and the oxygen of the potash bringing the heavy metal to a higher state of oxidation (Boudault, J. Pharm. [3] vii. 437); e.g.



The action may be produced by adding to the solution of the red salt either the hydrated oxide, together with potash, or a mixture of the salt of the heavy metal with excess of potash.—A solution of *chromic oxide* in potash boiled with the solution of the red salt, yields chromate and ferrocyanide of potassium.—*Hydrated manganous oxide* with potash, or a manganous salt with excess of potash, yields peroxide of manganese, even at ordinary temperatures; if the potash is in large excess, the peroxide produced is crystalline; but if the manganous oxide is in larger proportion, brown-red manganoso-manganic oxide is produced.—*Protoxide of lead* dissolved in potash, or a lead-salt supersaturated with potash, yields a precipitate of brown peroxide of lead, which is generally crystalline, or of red lead, if the lead-oxide is present in larger proportion.—*Stannous salts* also convert the red salt mixed with potash into the yellow salt.—But the *protoxides of cobalt and nickel* are not brought to a higher state of oxidation, even by boiling with a mixture of potash and the red salt.—*Silver and gold salts*, on the other hand, exhibit a different reaction with potash and the red prussiate; for they yield, on boiling, a precipitate of ferric oxide, while ferrocyanide of potassium and cyanide of silver and potassium, or cyanide of gold and potassium, remain in solution. 14.—*Sulphydric acid* decomposes the red prussiate dissolved in water into yellow prussiate, ferroproussic acid, and sulphur (Williamson, Ann. Ch. Pharm. lviii. 237):



15. *Selenydric acid* and *phosphoretted hydrogen* likewise impart to the solution of the red prussiate the property of forming a blue precipitate with ferric salts; and the same change is produced, though more slowly, by *tellurhydric acid*, *arsenetted hydrogen*, and *antimonetted hydrogen* gases (Schönbein).—16. *Ammonia* converts the aqueous solution of ferricyanide of potassium into ferrocyanide of potassium and ferrocyanide of ammonium, with evolution of nitrogen (Monthiers, J. Pharm. [3] xi. 254):



17. Many other deoxidising agents likewise impart to the aqueous solution of ferricyanide of potassium the property of forming a blue precipitate with ferric salts. The deoxidising agents which produce these effects are: *Phosphorus*, which acts but slowly;—*phosphorous acid* and the *hypophosphites*;—*sulphurous acid*, which is thereby converted into sulphuric acid, and *sulphites*, which are transformed into sulphates;—*nitric oxide gas*, and even *fuming nitric acid*, whereas nitrous oxide exerts no reducing action.

18. Similar effects are likewise produced by various metals: viz. *arsenic*, *antimony*, *tin*, *bismuth*, *lead*, *iron* and *zinc*, more slowly by *copper*, *cadmium*, *mercury* and *silver*. According to Schönbein, iron and zinc, immersed in the aqueous solution of red prussiate in a close vessel, often remain bright for weeks, whereas, in contact with the air, the liquid becomes lighter in colour, and ferrocyanide of potassium is formed, together with an insoluble ferrocyanide.

19. The reduction of red to yellow prussiate is likewise produced by many *organic substances*, e.g. by formic, acetic, citric, tartaric, and uric acids, creosote, cinchonine, and morphine, not by quinine or strychnine (Boudault). Ether, alcohol, and sugar do not easily reduce the aqueous solution of the red prussiate alone, but much more quickly on addition of a ferric salt, in which case prussian blue is precipitated. Oxalic

acid is not oxidised by the aqueous solution of red prussiate; indeed, its presence actually prevents the reduction which would otherwise be effected by nitric oxide, sulphydric acid, uric acid, or sugar. (Schönbein.)

All these reductions take place much more quickly in an alkaline than in a neutral solution of the red prussiate. In the alkaline solution, sulphur and phosphorus, and their lower oxides, are quickly converted into sulphuric and phosphoric acid respectively; iodine into iodic acid; iodide and sulphide of potassium also reduce the red prussiate to the yellow; oxalic acid is converted into carbonic acid; cyanide of potassium into cyanate; sugar, gum, starch, alcohol, and even paper, into carbonic acid and water. Indigo is bleached by it, a reaction which has been applied by Mercer (Phil. Mag. [3] xxxi. 126) in calico-printing. Cotton dyed with indigo and saturated with red prussiate is instantly bleached on immersion in potash-ley.

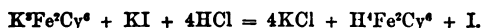
Ferricyanide of potassium forms, with the solutions of many of the *heavy metals*, precipitates which exhibit very characteristic colours (p. 244); hence this salt, as well as the yellow prussiate, is a valuable reagent in chemical analysis. In dyeing and calico-printing, it is used, either alone or mixed with ferrous salts, for the production of blue colours on wool and cotton; for this purpose the so-called "blue powder," obtained by evaporating the mother-liquors of red prussiate is often made available.

*Estimation of Ferricyanide of Potassium.*—Ordinary red prussiate is generally contaminated with chloride of potassium and with yellow prussiate, the latter being recognisable by the blue precipitate which it forms with ferric salts. For determining the proportion of real ferricyanide in a commercial sample of red prussiate, the following methods may be used:

1. Brunquell converts the ferricyanide of potassium into ferrocyanide, and estimates the latter by a standard ferric solution in the manner already described (p. 242). 7.99 grms. of the red prussiate are dissolved in water; and the liquid is boiled with addition of a few grms. of sulphite or hyposulphite of sodium, filtered, if a precipitate forms, and tested with the graduated ferric solution, 1 cc. of which corresponds to 1 per cent. of ferricyanide of potassium.

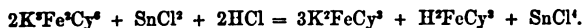
2. De Haen mixes 10 cc. of a solution of a red prussiate containing 20 grms. in a litre, with 5 to 8 cc. of strong potash-ley, and heats the liquid, after addition of 0.5 gm. finely pulverised protoxide of lead, which is thereby converted into peroxide. After dilution with water, filtering, and acidulation with hydrochloric acid, a graduated solution of *permanganate of potassium* (see p. 242) is added till the liquid becomes clear and of a decided reddish-yellow colour. If the sample of red prussiate originally contained yellow prussiate, the proportion of the latter is determined in a second sample by heating with the permanganate solution without addition of oxide of lead.

3. Ferricyanide of potassium mixed with *iodide of potassium and hydrochloric acid* yields ferroproussic acid, chloride of potassium, and free iodine:



Consequently 1 at., or 127 pts., iodine corresponds to 1 at., or 329 pts., ferricyanide of potassium. To apply this reaction volumetrically, 10 cc. of a solution of red prussiate (containing from 0.2 to 0.4 grms. of the salt) are mixed with 10 cc. of a solution of iodide of potassium (containing 1 gm. of the iodide), and strong hydrochloric acid is added as long as the solution is thereby rendered darker in colour by separation of iodine. The free iodine is then estimated by Bunsen's method with sulphurous acid (see ANALYSIS, VOLUMETRIC, i. 265). Lenssen (Ann. Ch. Pharm. xci. 240.)

4. Wallace (Chem. Soc. Qu. J. vii. 77) determines the amount of ferricyanide by the quantity of *stannous chloride* required to convert it into ferrocyanide of potassium or ferroproussic acid. The reaction is as follows:



100 grains of pure ferricyanide of potassium are dissolved in  $1\frac{1}{2}$  oz. water and  $\frac{3}{4}$  oz. strong hydrochloric acid, and solution of stannous chloride (of specific gravity 1.046) is added till the liquid exhibits a decided violet or blue without any shade of green colour. By treating the sample of red prussiate to be examined with the solution of stannous chloride thus standardised, the amount of pure ferrocyanide contained in it is determined.—5. Greater exactness appears to be attained by the following process given by Leesching (Jahresber. d. Chem. 1853, 681), in which an alkaline solution of the ferricyanide is mixed with a solution of *sulpharsenate of sodium*, till the liquid becomes nearly colourless and the precipitated sulphur is perfectly white. The reaction is expressed by the equation:



According to this equation, 100 pts. ferricyanide of potassium decompose 20.6 pts.



crystallised sulpharsenate of sodium,  $2\text{Na}^+\text{AsS}^4 + 15\text{aq.}$  100 grains of the ferricyanide are dissolved in 2 oz. of water, and to this solution is gradually added a standard solution containing 20 grains (more exactly 20.6 grains) of sulpharsenate of sodium and 40 to 60 grains dry carbonate of potassium or sodium in 200 burette-divisions\*, so that one division of this solution corresponds to  $\frac{1}{2}$  per cent. ferricyanide of potassium. The standard solution is gradually added till the liquid has become quite white, and a few drops of it no longer destroy the red colour of a decoction of cochineal. (Handw. d. Chem. 2<sup>te</sup> Aufl. ii. [2] 212.)

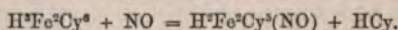
*Ferricyanide of Potassium and Barium*,  $\text{KBa}^+\text{Fe}^3\text{Cy}^6 + 3\text{aq.}$ , is obtained by passing chlorine into a solution of ferrocyanide of potassium and barium, expelling the excess of chlorine by heat, adding a little alcohol, separating the resulting blue precipitate by filtration, and leaving the filtrate to evaporate. The first crystals deposited from the solution (larger than those of ferrocyanide of potassium, which afterwards separate) consist of ferricyanide of potassium and barium; they are short hexagonal prisms, of a deep red colour, and permanent in the air. (Laurent, Compt. chim. 1849, p. 324.)

*Ferricyanide of Sodium*,  $\text{Na}^+\text{Fe}^3\text{Cy}^6 + \text{aq.}$ , prepared, like the potassium-salt, by the action of chlorine on the ferrocyanide, forms ruby-coloured right four-sided prisms, which deliquesce when exposed to the air, dissolve in 5.3 pts. of cold, and 1.25 pts. boiling water. (Kramer, J. Pharm. xv. 98; Bette, Ann. Ch. Pharm. xxiii. 117.)

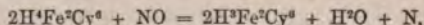
*Ferricyanide of Sodium and Potassium*,  $\text{Na}^+\text{K}^+\text{Fe}^3\text{Cy}^{12}$ , is deposited from a mixture of the solutions of ferrocyanide of potassium and ferricyanide of sodium, in fine cubic crystals of a garnet-red colour. The solution once also deposited large black-brown hydrated crystals, containing 6 at. water, and having the form of hexagonal prisms, with angles of  $120^\circ$ ; but on redissolving them in water, the solution yielded the cubic anhydrous crystals. The hydrated crystals give off their water at a temperature somewhat above  $100^\circ\text{C.}$ , decrepitating and falling to powder at the same time. (Laurent, loc. cit.)

#### Nitroferricyanides.

*Nitroprussides, Nitroprussiates.* (Playfair, Phil. Mag. [3] xxxvi. 197, 271, 348. —Gerhardt, Compt. chim. 1850, p. 147; *Traité*, i. 344.—Ky d, Ann. Ch. Pharm. lxxiv. 340.)—These compounds, discovered by Playfair in 1850, are produced by the action of nitric acid on the ferro- or ferri-cyanides of the alkali-metals, or by that of nitric oxide on ferro- or ferri-cyanide of hydrogen. Their composition is not yet established with certainty. Playfair represented them by the general formula  $\text{M}^n.\text{Fe}^x\text{Cy}^y(\text{NO})^z$ , or  $\text{M}^{10}.\text{Fe}^{10}\text{Cy}^{24}(\text{N}^2\text{O})^3$ , in which the cyanogen is supposed to be partly replaced by nitrous oxide; but the formula most generally received is that proposed by Gerhardt, viz.  $\text{M}^2.\text{Fe}^2\text{Cy}^3(\text{NO})$ , in which 1 at. cyanogen in  $\text{Fe}^2\text{Cy}^6$  is supposed to be replaced by nitric oxide. According to this formula, the formation of nitro-ferricyanide of hydrogen by the action of nitric oxide on *ferricyanide of hydrogen* is represented by the equation,



When nitric oxide is passed into a warm aqueous solution of *ferrocyanide of hydrogen* (or of ferrocyanide of potassium mixed with a sufficient quantity of an acid to convert it into ferrous acid), the gas is rapidly absorbed,—the ferrocyanide is converted into ferricyanide:



the change being indicated by the deep blue precipitate which the liquid then gives with ferrous salts,—and afterwards the ferricyanide is converted into nitroferricyanide as above, the liquid giving, with ferrous salts, precipitates of a paler and paler colour, and ultimately of a clear salmon tint. It then contains nitroferricyanide of hydrogen (nitroprussic acid), which will yield the nitroferricyanides of the different metals by neutralisation.

When nitric acid is added to a solution of *ferrocyanide of potassium*, this salt is first converted into ferricyanide by abstraction of 1 at. potassium (p. 243), and the nitric acid is at the same time reduced to nitric oxide, which, however, does not escape as gas, unless the action is very violent, but is employed in converting the ferricyanide into nitroferricyanide as above. The action is accompanied by evolution of hydrocyanic acid and nitrogen, as shown by the equations above given, also of carbonic acid,

\* Or 5 grms. of ferricyanide are dissolved in 50 cc. water, and to the liquid is added a standard solution containing in 200 burette-divisions 1.03 gr sulpharsenate of sodium, and 2 or 3 grms. carbonate of potassium or sodium.

cyanogen, and an extremely pungent vapour, probably cyanic acid, these latter being secondary products, resulting from the action of the nitric acid on the hydrocyanic acid.—[Respecting the formation of nitroferri-cyanides from the so-called *nitro-sulphurets of iron*, see Roussin (Ann. Ch. Phys. [3] lii. 285).]

*Preparation.*—The nitroferri-cyanides of potassium and sodium are obtained as follows: 422 gr. (2 at.) pulverised ferrocyanide of potassium is mixed with 5 at. commercial nitric acid diluted with its own bulk of water (the strength being determined by an alkalimetric process). One-fifth of this quantity (1 at.) of acid is actually sufficient to transform the ferrocyanide into nitroferri-cyanide, but the use of the larger quantity is found to give the best results. The acid is poured all at once upon the ferrocyanide, the cold produced by the mixing being sufficient to moderate the action. The mixture first assumes a milky appearance; but after a little while the salt dissolves, forming a coffee-coloured solution, and the gases above-mentioned are disengaged in abundance. When the salt is completely dissolved, the solution is found to contain ferri-cyanide (red prussiate) of potassium, mixed with nitroferri-cyanide and nitrate of the same base. It is then immediately decanted into a large flask, and heated over the water-bath; it continues to evolve gas, and, after a while, no longer yields a dark blue precipitate with ferrous salts, but a dark green or slate-coloured precipitate. It is then removed from the fire, and left to crystallise, whereupon it yields a large quantity of crystals of nitre, and more or less of oxamide. The strongly coloured mother-liquid is then neutralised with carbonate of potassium or sodium, according to the salt to be prepared, and the solution is boiled, whereupon it generally deposits a green or brown precipitate, which must be separated by filtration. The liquid then contains nothing but nitroferri-cyanide and nitrate of potassium or sodium. The nitrates being the least soluble, are first crystallised out; and the remaining liquid, on further evaporation, yields crystals of the nitroferri-cyanide. The sodium-salt crystallises most easily.

The insoluble nitroferri-cyanides, those of iron, copper, silver, zinc, &c., are obtained by precipitating the solution of the potassium or sodium salt, with solutions of the respective metals; and the ammonium, barium, calcium, and magnesium salts, which are soluble, by decomposing the iron or copper salt with a solution of caustic ammonia, baryta, or lime. (Playfair.)

*Properties and Reactions.*—The nitroferri-cyanides are in general strongly coloured. The ammonium, potassium, sodium, barium, calcium, and lead salts, are of a dark red or ruby colour; they dissolve easily in water, forming red solutions, from which they are not precipitated by alcohol. The soluble salts crystallise with facility. The copper, iron, cobalt, nickel, zinc, and silver salts, are nearly or quite insoluble in water.

The following are the most characteristic reactions of soluble nitroferri-cyanides.

With the Sulphides of the Al-

kali-metals . . .	Splendid but transient purple colour.
„ Sulphydic acid . . .	Formation of prussian blue, together with a ferrocyanide and a peculiar compound.
„ Neutral Lead-salts . . .	No change.
„ Basic „ . . .	White precipitate, after some time, from strong solutions.
„ Mercuric salts . . .	No change.
„ Stannous and Stannic salts . . .	No change.
„ Zinc-salts . . .	Light salmon-coloured precipitate.
„ Cupric salts . . .	Light green precipitate.
„ Cobalt-salts . . .	Flesh-coloured precipitate.
„ Ferrous salts . . .	Salmon-coloured precipitate.
„ Ferric salts . . .	No change.
„ Caustic alkalis . . .	Red coloration, changing to orange.

The most characteristic reaction of the nitroferri-cyanides is the splendid purple colour which they exhibit with *alkaline sulphides*: it is extremely delicate, and serves to detect the minutest portion either of a sulphide or of a nitroferri-cyanide. Oppenheim (J. pr. Chem. lxxxi. 305) recommends it for the detection of small quantities of free alkalis or alkaline earths in solution, a few bubbles of sulphydic acid gas being passed through the liquid, and then a few drops of solution of nitroferri-cyanide of sodium added. The purple colour is not, however, permanent, the compound being quickly resolved into other products, including hydrocyanic acid, ammonia, nitrogen, oxide of iron, a ferrocyanide, a sulphocyanate, and perhaps a nitrate. The purple compounds may be isolated by operating with alcoholic solutions; it is then blue, and appears to be simply a compound of nitroferri-cyanide and sulphide.

The soluble nitroferri-cyanides are decomposed by *sulphydic acid* gas, yielding oxide of iron, prussian blue, sulphur, a ferrocyanide, and a peculiar sulphur-compound.



The nitroferri-cyanides are decomposed by boiling with *alkalis*, yielding oxide of iron, free nitrogen, a ferrocyanide, and perhaps a nitrite. An excess of ammonia gradually decomposes them, even in the cold, nitrogen being evolved, and a black uncrystallisable substance finally remaining.

Nitroferri-cyanides are not sensibly affected by *sulphurous acid*, *sulphites*, or *hypo-sulphites*; but they are decomposed by boiling with strong *sulphuric acid*, the liquid during the decomposition exhibiting the peculiar purple colour which indicates the presence of a sulphide. *Chlorine* exerts no action on the nitroferri-cyanides. *Prussian blue* dissolves in the solutions of certain nitroferri-cyanides, with a fine blue colour.

Some of the nitroferri-cyanides are very permanent, their solutions undergoing no change either by exposure to the air, or by the action of heat. Several, on the contrary, especially the nitroferri-cyanides of hydrogen, ammonium, barium, and calcium, undergo partial decomposition when their solutions are long kept, and rapid alteration when boiled, depositing prussian blue or oxide of iron.

*Nitroferri-cyanide of Ammonium*,  $(\text{NH}_4)^2\text{Fe}^2\text{Cy}^3(\text{NO}) + \text{aq.}$ , is very unstable, depositing prussian blue when boiled, and then yielding by concentration rhombic crystals of a slightly altered salt. Dominant faces,  $\infty\text{P} \cdot \infty\text{P}\infty \cdot \text{P}\infty \cdot \text{oP}$ . Inclination of  $\infty\text{P} : \infty\text{P} = 91^\circ 56'$ ;  $\text{P}\infty : \infty\text{P}\infty$  in the macrodiagonal principal section =  $69^\circ 45'$ . (Miller: see *Playfair's Memoir*.)

*Nitroferri-cyanide of Barium*,  $\text{Ba}^2\text{Fe}^2\text{Cy}^3(\text{NO}) + 2 \text{aq.}$ , crystallises in vacuo in fine octahedral crystals of a dark red colour. The crystals belong to the dimetric system, exhibiting the dominant faces  $\text{P} \cdot \text{oP} \cdot \infty\text{P}\infty$ . Inclination of  $\text{P} : \text{P}$  in the terminal edges =  $120^\circ 30'$ ;  $\text{P} : \text{oP} = 135^\circ 25'$  (Miller). Concentrated solutions sometimes yield flattened prisms which appear to be another hydrate. This salt is very soluble in water; the solution when boiled deposits a brown precipitate. The crystallised salt dried in vacuo gives off from 14.9 to 15.2 p. c. water at  $100^\circ\text{C}$ .

*Nitroferri-cyanide of Calcium*,  $\text{Ca}^2\text{Fe}^2\text{Cy}^3(\text{NO}) + x \text{aq.}$ , forms shining dark red monoclinic prisms, with the dominant faces  $\infty\text{P} \cdot \infty\text{P}\infty \cdot \text{oP}$ . Inclination of  $\infty\text{P}\infty : \text{oP} = 82^\circ$ ;  $\infty\text{P} : \infty\text{P}$  in the orthodiagonal principal section =  $140^\circ$ . (Miller.)

The *copper-salt* is a pale green precipitate insoluble in water, and acquiring a slate colour when exposed to light in the moist state.

*Nitroferri-cyanide of Hydrogen* or *Nitroprussic acid*,  $\text{H}^2\text{Fe}^2\text{Cy}^3(\text{NO}) + \text{aq.}$ , is obtained by decomposing the silver-salt with an equivalent quantity of hydrochloric acid, or the barium-salt with an equivalent quantity of sulphuric acid. The red strongly acid solution yields, by evaporation in vacuo, dark red, very deliquescent, oblique prisms, part of the acid, however, decomposing at the same time, with formation of hydrocyanic acid and oxide of iron. The aqueous solution is not precipitated by ether.

*Nitroferri-cyanide of Iron (ferrous)* is a salmon-coloured precipitate, nearly insoluble in pure water, more soluble in water acidulated with nitric acid. It is decomposed by caustic alkalis, with separation of oxide of iron and formation of a soluble nitroferri-cyanide, a dark-coloured basic iron-salt being, however, formed previous to complete decomposition. After drying at  $32^\circ\text{C}$ . it loses about 20 per cent. more water when heated to  $100^\circ$ .

*Nitroferri-cyanide of Potassium*,  $\text{K}^2\text{Fe}^2\text{Cy}^3(\text{NO})$ , forms dark red oblique prisms, more soluble than the sodium-salt, and less easy to crystallise. The crystals are monoclinic. Dominant faces  $\infty\text{P} \cdot [\infty\text{P}\infty] \cdot -\text{P} \cdot -\text{P}\infty \cdot [\frac{1}{2}\text{P}\infty]$ . Inclination of  $\infty\text{P} : [\infty\text{P}\infty] = 130^\circ 14'$ ;  $-\text{P} : [\infty\text{P}\infty] = 125^\circ 55'$ ;  $-\text{P}\infty$  : principal axis =  $67^\circ 56'$ . The salt is very deliquescent, and acquires a faint green tint when exposed to light. Its solution after a while deposits prussian blue.

On mixing the aqueous solution of this salt with twice its volume of alcohol, and then adding caustic potash, a light yellow curdy precipitate is formed, consisting of a basic salt,  $\text{K}^2\text{Fe}^2\text{Cy}^3(\text{NO}) \cdot 2\text{KHO}$ .

*Nitroferri-cyanide of Silver*,  $\text{Ag}^2\text{Fe}^2\text{Cy}^3(\text{NO})$ , is a flesh-coloured precipitate, insoluble in water, alcohol, and nitric acid.

*Nitroferri-cyanide of Sodium*,  $\text{Na}^2\text{Fe}^2\text{Cy}^3(\text{NO}) + 2 \text{aq.}$ , is prepared as described on page 251. The dark red solution which remains after the nitrates of potassium and sodium have crystallised out, yields by evaporation, prismatic crystals, which must be taken out of the liquid, dissolved in water, and left to crystallise by cooling. The object of taking the crystals out of the hot solution, is to obtain them free from nitrates, which are more soluble in hot water than the nitroferri-cyanide.

The crystals are large ruby-coloured prisms, bearing considerable resemblance to ferri-cyanide of potassium crystallised from an alkaline solution. The salt is not deliquescent, dissolves in  $\frac{2}{3}$  pts. of water at  $15^\circ\text{C}$ ., and in a smaller quantity of hot water. It does not lose weight at  $100^\circ\text{C}$ .



The crystals belong to the trimetric system. Dominant faces,  $\infty P$ .  $\infty P_{\infty}$ .  $\infty \bar{P}_{\infty}$ .  $\bar{P}_{\infty} : \bar{P}_{\infty}$ . Inclination of  $\infty P : \infty P = 105^{\circ} 17'$ ;  $\bar{P}_{\infty} : \bar{P}_{\infty}$  in the brachydiagonal principal section =  $136^{\circ} 32'$ ;  $P_{\infty} : \bar{P}_{\infty}$  in the macrodiagonal principal section =  $124^{\circ} 52'$ . (Miller.)

A solution of the salt exposed to sunshine becomes coloured, deposits prussian blue, and gives off nitric oxide. (Overbeck, Pogg. Ann. lxxvii. 110.)

**CYANIDE OF LEAD.** Hydrocyanic acid does not precipitate either the nitrate, the neutral acetate, or the basic acetate of lead. Cyanide of ammonium forms with the neutral acetate a slight yellowish precipitate.

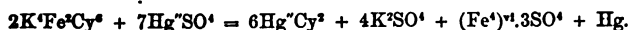
*Oxycyanide of Lead.* On mixing a solution of basic acetate of lead with ammonia, and then adding hydrocyanic acid, a white precipitate is formed, containing  $PbCy.PbHO$ , according to Kugler (Ann. Ch. Pharm. lxi. 63),—whose formula does not, however, agree well with his analysis,—and  $PbCy.Pb^2O$ , according to Erlenmeyer (J. pr. Chem. xlviii. 356).

**CYANIDE OF MAGNESIUM.** Soluble salt produced by dissolving recently precipitated magnesia in hydrocyanic acid. It is decomposed by the carbonic acid of the air.

**CYANIDES OF MANGANESE.** (Rammelsberg, Pogg. Ann. xlii. 117.—Haidlen and Fresenius, Ann. Ch. Pharm. xlii. 132.—Balard, Compt. rend. xix. 909.)—Cyanide of potassium forms with manganous salts a bulky reddish-white precipitate, which quickly turns brown in contact with the air. It is decomposed by strong acids, and dissolves in alkaline cyanides, the solutions when exposed to the air being converted into manganicyanides,  $R^2Mn^2Cy^6$ , salts analogous in composition to the ferricyanides.

*Manganicyanide of potassium*,  $K^2Mn^2Cy^6$ , obtained in this manner, forms brown-red anhydrous needles, isomorphous with the ferricyanide. In contact with the air the crystals turn brown, and their aqueous solution becomes turbid and gradually deposits the manganese in the form of a black hydrate, the decomposition being accelerated by dissolving and evaporating several times. Acids decompose the salt, eliminating hydrocyanic acid. Alkalis do not act upon it. Sulphide of ammonium slowly precipitates a portion of the manganese. The crystals are decomposed by water and by alcohol, so that it is necessary to dissolve them in cyanide of potassium. The solution gives, with various metallic salts, precipitates of analogous composition, and for the most part easily decomposable. The precipitate formed with *ferrous salts* has a cobalt-blue colour; those with *zinc* and *cadmium* salts are rose-coloured; with *lead-salts*, brown; with *silver-salts* from neutral solutions, yellowish-brown; in presence of free acid, scarlet, but becoming brown by washing.

**CYANIDE OF MERCURY.**  $HgCy$  or  $Hg^2Cy^2$ , according as mercury is regarded as monatomic (= 100) or diatomic (= 200). This salt, discovered by Scheele (*Opuscula*, ii. 159) is obtained by the action of mercuric sulphate on ferrocyanide of potassium, or of mercuric oxide on hydrocyanic acid, or of the same oxide on prussian blue (p. 228).—1. One part of ferrocyanide of potassium is boiled for a quarter of an hour with 2 pts. mercuric sulphate and 8 pts. water; the deposit is separated by filtration, and the liquid evaporated to the crystallising point (Desfossez, J. Chim. méd. vi. 261). Theoretically, 100 pts. ferrocyanide require 245 pts. mercuric sulphate, and yield 179 pts. mercuric cyanide:



2. Mercuric oxide is digested with dilute hydrocyanic acid, till the odour of the acid is no longer perceptible, and the solution is left to evaporate.—3. Four pts. pulverised prussian blue and 3 pts. mercuric oxide are boiled with 40 pts. water; the liquid is filtered as soon as the solid matter has acquired a light brown colour; the residue is boiled with a fresh quantity of water; the second filtrate added to the former; and the whole evaporated to the crystallising point.

Cyanide of mercury crystallises in forms belonging to the dimetric system, colourless, transparent, permanent in the air, having a nauseous metallic taste, and very poisonous. They are anhydrous. The salt dissolves in 8 pts. of cold water; it is less soluble in hydrated alcohol, quite insoluble in absolute alcohol.

For the primary form P, the length of the principal axis is 0.4596. The angle P : P in the terminal edges =  $134^{\circ} 40'$ ; in the lateral edges  $66^{\circ} 2'$ . P is for the most part sphenoidically hemihedral, and the character of the crystals varies considerably, according to the manner in which they are obtained. By spontaneous evaporation, quadratic sphenoids (p. 136), are often obtained, either perfectly developed, or having their lateral edges truncated by the faces  $\infty P_{\infty}$  as in *fig.* 368. By rapid cooling prismatic crystals are produced, in which the face  $\infty P_{\infty}$  predominates (*figs.* 365, 366).

In *fig. 365*, the prism  $\infty P\infty$  is bevelled by the faces  $\frac{P}{2}$ , which are set alternately on the prismatic edges above and below. In *fig. 366*, the prism exhibits an oblique

Fig. 365.

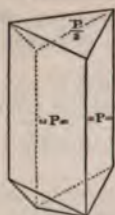
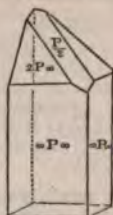


Fig. 366.



termination, one only of the two upper faces  $\frac{P}{2}$  being distinctly formed, while the other is either very subordinate or not present at all: on the other hand, two faces are present belonging to the pyramid  $2P\infty$  (the next acuter to the primary form  $P$ ); they rest symmetrically on the prismatic faces  $\infty P\infty$ , and the terminal edge in which two of them would meet is truncated by the faces  $\frac{P}{2}$ .

A solution of the salt slowly evaporated often yields crystals of different form (*fig. 367*), with faces of the sphenoid  $\frac{P}{2}$  resting alternately on the edges of the prism  $\infty P\infty$ , and faces of the pyramid  $2P\infty$  (of which, however, only four are present) resting on the faces of the same prism. The two upper (and likewise the two lower) faces  $2P\infty$  are separated from one another by  $\infty P$  and by two faces of an obtuser pyramid of

Fig. 367.

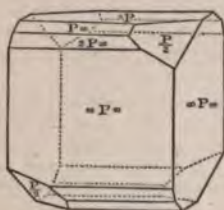
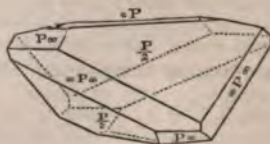


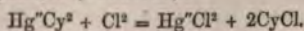
Fig. 368.



the second order, which are rendered dull by deep striation, and likewise rounded, so that they cannot be accurately determined, but appear to belong to  $P\infty$ . More frequently, however, the crystals obtained by slow evaporation have the form shown in *fig. 368*, the faces  $\frac{P}{2}$  predominating, their lateral edges truncated by  $\infty P\infty$ , and each terminal edge replaced by  $\infty P$  and by two faces of the pyramid of the second order, which is probably  $P\infty$ . (*Kopp's Krystallographie*, p. 150.)

*Decompositions.*—1. Cyanide of mercury when heated, turns black, softens, and yields, if perfectly dry, nothing but cyanogen gas and mercury; part of the cyanogen is, however, converted into the isomeric compound, paracyanogen, which remains in the form of a black, very light, coaly mass, the quantity thus altered being greater as the heat is stronger; at the same time, a small quantity of cyanide of mercury sublimes undecomposed. If the cyanide of mercury is moist, it yields carbonic acid, ammonia, hydrocyanic acid, and mercury. (Gay-Lussac.)

2. Dry cyanide of mercury is not decomposed by dry chlorine gas in the dark; but in strong sunshine it undergoes decomposition, emitting the odour of chloride of cyanogen (Gay-Lussac), and in ten days, yields protochloride of mercury and a yellow oily liquid (Serullas, *Ann. Ch. Phys.* xxxv. 293).—Cyanide of mercury exposed in the moist state to chlorine gas, is converted in the dark into protochloride of mercury and volatile chloride of cyanogen (Serullas):



But in strong sunshine — its temperature rising to 30° or 40° C. — it yields sal-ammoniac, protochloride of mercury, the above-mentioned yellow oil, a small quantity of volatile chloride of cyanogen, and a trace of carbonic acid. If the cyanide of mercury is completely dissolved in water, chlorine in sunshine produces a large quantity of the yellow oil and a small quantity of volatile chloride of cyanogen (Serullas). According to Bouis (Ann. Ch. Phys. [3] xx. 446; Jahresber. d. Chem. 1847—8, 486), a hot saturated solution of cyanide of mercury treated with excess of chlorine in sunshine, is converted into chloride of mercury, hydrochloric acid, and sal-ammoniac, which remain dissolved in the water, together with chloride of cyanogen, carbonic acid, and nitrogen, which escape, and a yellow, oily liquid, to which Bouis assigns the formula  $C^*N^*Cl^{14}$ . A mixture of the aqueous solutions of cyanide of mercury and *chloride of lime*, which is clear at first, begins in a few minutes to emit white fumes, effervescing violently and giving off nitrogen, carbonic acid, and a small quantity of cyanogen; neither cyanic nor cyanuric acid is produced in this reaction (Liebig, Pogg. Ann. xv. 571).—3. *Bromine* at medium temperatures decomposes cyanide of mercury, with great evolution of heat, yielding protobromide of mercury and bromide of cyanogen (Serullas, Ann. Ch. Phys. xxxi. 100).—4. *Iodine*, even when triturated cold with cyanide of mercury, yields protiodide of mercury and iodide of cyanogen. (H. Davy, Porrett.)

5. When cyanide of mercury is distilled with  $\frac{1}{2}$  of its weight of *sulphur*, the mass fuses, gives off nitrogen, cyanogen, and vapour of sulphide of carbon; then becomes viscid, swells up, and leaves a black mass insoluble in water; and this, when further heated, yields nitrogen, cyanogen, sulphide of carbon, and cinnabar, while light yellow mercurous sulphocyanate remains, which at a higher temperature partly sublimes in the form of a yellow, sometimes translucent, crystalline mass, but is for the most part resolved into cyanogen gas and cinnabar (Berzelius).—6. Cyanide of mercury, gently heated with *phosphorus*, yields a white sublimate, perhaps a cyanide of phosphorus, having a pungent odour, and decomposed by water into phosphoric and hydrocyanic acids. The preparation of this substance is very difficult, generally giving rise to a violent explosion. (Cenedella, J. Pharm. xxi. 683.)

7. Cyanide of mercury is decomposed when heated with strong *sulphuric acid*, not by dilute sulphuric or by nitric acid. With *hydrochloric*, *hydrobromic*, *hydriodic*, and *sulphydic acids*, it yields hydrocyanic acid and a mercuric compound of the radicle of the acid. An excess of hydrochloric acid, aided by heat, may, however, decompose the resulting hydrocyanic acid into ammonia and formic acid, in which case the residue will consist of mercuric chloride and sal-ammoniac.

8. Cyanide of mercury heated with *sal-ammoniac* yields cyanide of ammonium and mercuric chloride, which unites with the sal-ammoniac if the latter is in excess.—9. With solution of *stannous chloride*, it yields hydrocyanic acid, and a black mixture of stannic oxide and mercury.—10. When shaken up with *iron filings* and dilute sulphuric acid, it yields hydrocyanic acid, metallic mercury, and ferrous *sulphate*.—11. With aqueous *trisulphide of potassium*, it yields mercuric sulphide and sulphocyanate of potassium :



Aqueous *alkalis* do not decompose cyanide of mercury, even at the boiling heat.

*Combinations.* a. With *Mercuric oxide*.—Warm aqueous cyanide of mercury dissolves a large quantity of mercuric oxide, forming an alkaline solution, which deposits small needles of oxycyanide of mercury,  $Hg^{\circ}Cy^2.Hg^{\circ}O$ , or  $(Hg^{\circ})^2.Cy^2O$ , sparingly soluble in cold, moderately soluble in boiling water, sparingly in hydrated alcohol.

b. With *Salts*.—Cyanide of mercury combines with a large number of salts, forming definite, soluble, crystalline compounds, which are obtained by evaporating the mixed solutions of the component salts. The greater number of them contain 1 at.  $Hg^{\circ}Cy^2$  (or 2 at.  $Hg^{\circ}Cy$ ), to 1 at. of the other salt, and these may likewise be obtained by dissolving 1 at. mercuric chloride, iodide, &c., in a solution of potassio-mercuric, sodio-mercuric cyanide, &c. For this reason Gauthier (Ann. Ch. Pharm. cvi. 241) regards them as compounds of mercuric chloride, iodide, &c., with double cyanides, e.g.,  $2(Hg^{\circ}Cy^2.KCl) = K^2Hg^{\circ}Cy^2.Hg^{\circ}Cl^2$ . The latter view receives some support from the fact that these double salts are decomposed by the weaker acids, such as arsenious and benzoic acid, with evolution of prussic acid, whereas cyanide of mercury itself is not decomposed by weak acids. The double salts of cyanide of mercury have been investigated chiefly by Brett (Phil. Mag. [3] xii. 235); Poggiale (Compt. rend. xxiii. 762); Caillot (Ann. Ch. Phys. [3] xix. 230); Custer (Arch. Pharm. [2] lvi. 1); Rammeisberg (Pogg. Ann. xlii. 131; lxxxv. 146); Darby (Chem. Soc. Qu. J. i. 23); L. Gmelin (*Handbook*, viii. 17).

1. With *Acetate of Sodium* :

$HgCy^2.2C^*H^3NaO + 7 aq.$  Once obtained from the mother-liquor of a solution of the two salts. (Custer.)



## 2. With Bromides :

$\text{HgCy}^2.\text{KBr}$ . Nacreous scales soluble in 13.4 pts. water  $18^\circ\text{C}$ ., and in less than 1 pt. boiling water. (Caillot, Brett.)

$\text{HgCy}^2.\text{NaBr}$ . Long flattened needles, very soluble in water.

$\text{HgCy}^2.\text{BaBr} + 3\text{aq.}$  Square tables with a strong lustre, and very soluble. (Caillot.)

$\text{HgCy}^2.\text{SrBr} + 3\text{aq.}$  Rhombic tablets, efflorescent and soluble. (Caillot.)

$\text{HgCy}^2.\text{CaBr} + \frac{5}{2}\text{aq.}$  Very soluble in water and in alcohol. (Custer.)

## 3. With Chlorides :

$\text{HgCy}^2.\text{NH}^4\text{Cl}$ . Silky needles, soluble in water and alcohol.  $\text{HgCy}^2.4\text{NH}^4\text{Cl}$ . Triangular laminæ which separate from the solution of the preceding salt.

$\text{HgCy}^2.\text{KCl}$ . Colourless scales, soluble in water and in alcohol. (L. Gmelin.)

$\text{HgCy}^2.\text{NaCl}$ . Silky flattened needles, soluble in water and in alcohol. (Brett, Poggiale.)

$\text{HgCy}^2.\text{BaCl} + 2\text{aq.}$  Oblique prisms, very soluble and efflorescent. (Brett.)

$\text{HgCy}^2.\text{SrCl} + 3\text{aq.}$  Silky, very soluble needles. (Brett, Poggiale.)

$\text{HgCy}^2.\text{CaCl} + 3\text{aq.}$  Efflorescent, very soluble needles. (Brett, Poggiale.)

$\text{HgCy}^2.\text{MgCl} + \text{aq.}$  Needles very soluble and slightly deliquescent. (Brett, Poggiale.)

$\text{HgCy}^2.\text{MnCl} + \frac{3}{2}\text{aq.}$  Four-sided prisms, very soluble. (Poggiale.)

$\text{HgCy}^2.\text{ZnCl} + 3\text{aq.}$  Right prisms, efflorescent and soluble in water. (Poggiale.)

$\text{HgCy}^2.4\text{CoCl} + 4\text{aq.}$  Reddish-yellow mammellated groups. (Poggiale.)

$\text{HgCy}^2.2\text{NiCl} + 6\text{aq.}$  Greenish blue, deliquescent. (Poggiale.)

$\text{HgCy}^2.\text{HgCl}^2$ . Four-sided prisms, permanent in the air. (Liebig, Schw. J. xlix. 253.—Poggiale.)

*Stannic chloride* appears also to unite with cyanide of mercury, forming a confusedly crystalline compound. *Stannous chloride* decomposes cyanide of mercury (p. 255).

## 4. With Chromates :

$\text{HgCy}^2.\text{KCrO}^2$ . Large laminæ of a light yellow colour, very soluble (Poggiale, Caillot and Podevin). It is obtained either by mixing the solutions of equal parts of cyanide of mercury and neutral chromate of potassium (Caillot and Podevin, J. Pharm. xi. 246), or by boiling basic mercuric chromate for some time with an equivalent quantity of potassio-mercuric cyanide (Geuther, Ann. Ch. Pharm. cvi. 241).—Another salt,  $3\text{HgCy}^2.4\text{KCrO}^2$ , is obtained by mixing the solutions of 1 pt. chromate of potassium and 3 pts. cyanide of mercury, and leaving the mixed solution to evaporate. It then yields, first crystals of cyanide of mercury, then red crystals of the double salt. If only 2 pts of mercuric cyanide are used to 1 pt. chromate, the first deposit of mercuric cyanide is but of small amount. (Darby, Rammelsberg.)

2( $\text{HgCy}^2.\text{AgCrO}^2$ ). $\text{Cr}^2\text{O}^3$ , or  $2\text{HgCy}^2.(\text{Ag}^2\text{O}.2\text{Cr}^2\text{O}^3)$ , is obtained in splendid red needles by mixing the solution of the preceding salt with nitrate of silver, as long as a precipitate continues to form, then heating the liquid nearly to the boiling point, adding sufficient nitric acid to dissolve the whole, and leaving the solution to cool. (Darby.)

## 5. With Cyanides :

$\text{HgCy}^2.2\text{KCy} = \text{K}^2\text{Hg}^2\text{Cy}^4$ , forms regular octahedrons, colourless, permanent in the air, soluble in cold water. (L. Gmelin.)

$3\text{HgCy}^2.\text{K}^4\text{Fe}^2\text{Cy}^6 + 4\text{aq.} = \text{K}^4(\text{Hg}^2)^2\text{Fe}^2\text{Cy}^{12} + 4\text{aq.}$  Pale yellow, rhombic tables, obtained by agitating a moderately concentrated solution of ferricyanide of potassium with metallic mercury; a precipitate of ferric oxide is first formed, mixed with mercury, and the yellowish filtrate yields the double salt by evaporation.

*Cyanide of mercury and sodium* crystallises in octahedrons. *Cyanide of mercury and zinc* is obtained as a white precipitate on adding a zinc-salt to the solution of cyanide of mercury and potassium. The corresponding *lead-compound* is a white precipitate obtained in like manner.

## 6. With Formates :

$\text{HgCy}^2.2\text{CH}(\text{NH}^4)\text{O}^2$  forms triangular prisms. (Poggiale.)

$\text{HgCy}^2.2\text{CHKO}^2$  forms shining scales. (Winckler, Repert. Pharm. xxxi. 459.)

## 7. With Hyposulphites :

$2\text{HgCy}^2.\text{K}^2\text{S}^2\text{O}^3$ . Large prisms, obtained by concentrating in vacuo the mother-liquor of the solution of the two salts in equivalent quantities. (Kessler, Pogg. Ann. lxxiv. 274.)

## 8. With Iodides :

$\text{HgCy}^2.\text{KI}$  forms colourless, nacreous, soluble prisms. (Caillot.)

$\text{HgCy}^2.\text{NaI} + 2\text{aq.}$  Silky prisms, very soluble in water and alcohol, giving off their water of crystallisation at  $100^\circ\text{C.}$  Mineral acids decompose them, precipitating mercuric iodide and evolving hydrocyanic acid. (Custer.)

$\text{HgCy}^2.\text{BaI} + 2\text{aq.}$  Square tables. (Custer.)

$\text{HgCy}^2.\text{SrI} + 3\text{aq.}$  Square tables. (Custer.)

$\text{HgCy}^2.\text{CaI} + 3\text{aq.}$  Very soluble silky tufts. (Poggiale.)

9. With Nitrates :

$\text{HgCy}^2.\text{AgNO}_3 + 2\text{aq.}$  Obtained by mixing mercuric nitrate with equivalent quantities of cyanide of silver and cyanide of mercury. It forms long slender needles, which melt above  $100^\circ\text{C.}$ , and then detonate. (Geuther.)

Cyanide of mercury forms with *mercuric nitrate*, a compound which crystallises in nacreous scales or colourless prisms.

10. With Sulphates :

$2\text{HgCy}^2.\text{Ag}_2\text{SO}_4 + \text{aq.}$  Colourless crystals obtained like the corresponding nitrate compound. (Geuther.)

11. With Sulphocyanates :

$\text{HgCy}^2.4\text{KCyS.}$  Obtained, by crystallising the two salts together, in large laminae or needles, colourless, sparingly soluble in cold, very soluble in boiling water. (Böckmann.)

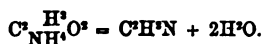
$\text{HgCy}^2.4\text{BaCyS.}$  Nacreous scales. (Böckmann, Ann. Ch. Pharm. xxii. 153.)

$\text{HgCy}^2.4\text{CaCyS.}$  Shining scales. (Böckmann.)

The *magnesium-salt* is a white crystalline powder. (Böckmann.)

Cyanide of mercury also forms definite compounds with *alkaloids*. (See the several *ALKALOIDS*.)

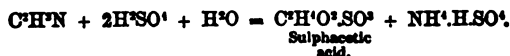
**CYANIDE OF METHYL.** *Acetonitrile.*  $\text{C}^2\text{H}^1\text{N} = \text{CH}^3.\text{CN} = \text{CH}^3.\text{Cy.}$ —This compound is obtained : 1. By distilling dry sulphomethylate of potassium with cyanide of potassium, adding chloride of calcium to the distillate, and distilling again at a gentle heat. The product is contaminated with hydrocyanic acid (Frankland and Kolbe, Chem. Soc. Mem. iii. 386; Ann. Ch. Pharm. lxx. 288).—2. By the action of cyanide of potassium on sulphate of methyl. The product is contaminated with cyanide and formate of ammonium; the latter impurity imparts to the product an intolerable taste and odour, and a highly poisonous action; it may be removed by boiling with mercuric oxide and then with phosphoric anhydride (Dumas, Malaguti, and Leblanc, Compt. rend. xxv. 474).—3. By distilling a mixture of phosphoric anhydride and crystallised acetate of ammonium :



The product is purified by digestion with a saturated solution of chloride of calcium and rectification over solid chloride of calcium and magnesium (Dumas, Compt. rend. xxxv. 383).—4. By distilling acetamide with phosphoric anhydride, washing the distillate with potash to remove hydrocyanic and acetic acids, and rectifying over phosphoric anhydride (Buckton and Hofmann, Chem. Soc. Qu. J. ix. 242).—5. Cyanide of methyl is found, together with the cyanides of ethyl and tetryl, among the products of the oxidation of gelatin by a mixture of acid chromate of potassium and sulphuric acid. Legumin treated in like manner appears also to yield a small quantity of it. (Fröhde, J. pr. Chem. lxxix. 303.)

Cyanide of methyl is a colourless liquid, which boils at  $77^\circ\text{C.}$  (Dumas), between  $77^\circ$  and  $78^\circ$  (Buckton and Hofmann), and mixes in all proportions with water. Vapour-density by experiment = 1.46, by calculation (2 vol.) = 1.42. It has an ethereal odour, somewhat like that of cyanogen, and a rather pungent aromatic taste; burns with a bright reddish-bordered flame. (Buckton and Hofmann.)

Boiled with aqueous *potash*, it gives off ammonia and forms acetate of potassium. *Chromic acid* and boiling *nitric acid* have no action upon it. *Potassium* acts violently upon it even in the cold, cyanide of potassium being formed, with rise of temperature, and a combustible gas evolved consisting of free hydrogen and carburetted hydrogen (Dumas). Heated with *fuming sulphuric acid*, it yields disulphometholic acid and sulphacetic acids :





## 258 CYANIDE OF NICKEL—CYANIDE OF NITROGEN.

The relative quantities in which these two acids are formed depends upon the temperature. If the materials are mixed so as to avoid heating as much as possible, scarcely any carbonic anhydride is evolved, and the chief product is sulphacetic acid; but if the temperature be considerably raised, carbonic anhydride is rapidly evolved and disulphometholic acid is produced. The latter stage of the reaction appears to consist in the resolution of the acetic acid,  $C^2H^3O^2$ , into carbonic anhydride and marsh-gas,  $CH^4$ , which then unites with 2 at.  $SO^3$ , forming disulphometholic acid. (Buckton and Hofmann, *loc. cit.*)

*Combinations.* a. With *Trichloride of Phosphorus*.  $C^2H^3N.PCl^3$ . (Henke, *Ann. Ch. Pharm.* cvi. 281.)—This compound, obtained by distilling acetamide with pentachloride of phosphorus, is a colourless, mobile, very pungent liquid, which boils at  $72^\circ C.$ , and takes fire in contact with a spirit-flame. Its vapour-density is anomalous, being 3.56 at  $95^\circ C.$ , 3.54 at  $87^\circ$ , and 2.4 at  $148^\circ$ . The medium number represents nearly a condensation to four instead of two volumes  $\left(\frac{41 + 137.5}{4} \times 0.0693 = 3.09\right)$ .

The anomaly probably arises, as in other similar cases, from the decomposition of the compound at the temperature at which the vapour-density is determined, into  $C^2H^3N$  and  $PCl^3$ , each of which occupies two volumes.

b. With *Metallic Chlorides*.—These compounds are formed by direct combination. The *antimony-compound*,  $C^2H^3N.SbCl^3$ , the formation of which is attended with great rise of temperature, is white, crystalline, and sublimes without decomposition. The *gold-compound*,  $C^2H^3N.AuCl^3$ , is a brownish-yellow powder. The *titanium-compound*,  $2C^2H^3N.TiCl^4$ , forms white, coherent, crystalline crusts, which may be sublimed. The *tin-compound*,  $2C^2H^3N.SnCl^4$ , is white, crystalline, and sublimes in arborescent formations. (Henke, *loc. cit.*)

c. With *Cyanide of Mercury*.  $C^2H^3N.2Hg^2Cy^2$ .—White crystalline mass, with vitreous lustre, produced by exposing pulverised cyanide of mercury to the vapour of cyanide of methyl. The compound gives off its cyanide of methyl when exposed to moist air, or when dried over sulphuric acid. Heated in a tube it turns black, and yields a sublimate of white crystals mixed with mercury. (O. Hesse, *Ann. Ch. Pharm.* ex. 202.)

*Cyanide of Trichloromethyl*, or *Chloracetonitrile*,  $CCl^3.CN$ , is obtained by distilling trichloracetate of ammonium, with phosphoric anhydride. It is a liquid of specific gravity 1.444, boiling at  $81^\circ C.$  With boiling potash, it yields ammonia and trichloracetate of potassium. It is violently attacked by potassium. (Dumas, Malaguti, and Leblanc, *Compt. rend.* xxv. 442.)

**CYANIDE OF NICKEL.**  $NiCy$ .—Nickel-salts form with cyanide of potassium a light apple-green precipitate, soluble in excess of cyanide of potassium. It turns brown when dried, giving off 19 per cent. water.

The double cyanides of nickel belong to the less stable class of double cyanides (p. 201), giving off prussic acid when heated with dilute acids.

*Cyanide of Nickel and Ammonium* is a somewhat unstable compound, obtained by dissolving cyanide of nickel in aqueous cyanide of ammonium, and leaving the solution to evaporate.

*Cyanide of Nickel and Barium* forms yellow crystals, which give off 20 per cent. water when heated. *Cyanide of Nickel and Calcium* forms yellow hydrated crystals. *Cyanide of Nickel and Cobalt* is a pale red precipitate, producing on mixing the solution of a cobalt-salt with cyanide of nickel and potassium. The corresponding *cupric salt* is an apple-green precipitate. The *ferrous salt* is a white precipitate. The *lead-salt* is a yellow crystalline powder, which separates after a while from a solution of acetate of lead mixed with cyanide of nickel and potassium.

*Cyanide of Nickel and Potassium*,  $K^2NiCy^4 + aq.$ —Obtained by dissolving cyanide or recently precipitated sulphide of nickel in cyanide of potassium. Crystallises in oblique rhomboidal prisms, having a yellow colour. The aqueous solution yields with dilute acids a precipitate of cyanide of nickel. According to Rammelsberg (*Pogg. Ann.* xlii. 114) and Balard (*Compt. rend.* xix. 999) the crystals contain 6.61 per cent. water, which they give off at  $200^\circ C.$

*Cyanide of Nickel and Sodium*,  $Na^2Ni^2Cy^4 + 3aq.$ , forms yellow hexagonal prisms, which give off their water at  $100^\circ C.$

**CYANIDE OF NITROGEN** is said to be produced when a solution of cyanide of potassium is poured upon chloride of nitrogen. The gas thereby evolved, which explodes in contact with phosphorus, and is said to contain cyanide of nitrogen, is probably nothing but nitrogen containing vapour of chloride of nitrogen. Iodide of nitrogen is dissolved by cyanide of potassium without colour, and probably with for-



mation of iodoform, formate of potassium, and iodide of ammonium. (Millon, Ann. Ch. Phys. [3] lix. 75.)

**CYANIDES OF OSMIUM.** (Claus, *Beiträge zur Chemie der Platinmetalle*, Dorpat. 1854. — C. A. Martius, *Inauguraldissertation*, Göttingen, 1860; Ann. Ch. Pharm. cxvii. 357; Jahresber. d. Chem. 1860, p. 233.)—The only cyanide of osmium which appears to have been obtained in the free state, is the proto-cyanide  $\text{OsCy}$ ; it is separated as a dark violet-coloured precipitate, when an osmiocyanide is boiled for some time with strong hydrochloric acid; also when moist osmiocyanide of hydrogen is exposed to the air.

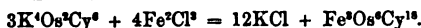
Proto-cyanide of osmium unites with the more basic cyanides, forming a class of double salts, the **OSMIOCYANIDES**,  $\text{M}^{\text{I}}\text{Os}^{\text{II}}\text{Cy}^{\text{I}} = 4\text{M}^{\text{I}}\text{Cy} \cdot 2\text{OsCy}$ , analogous to the ferro-cyanides, and exhibiting somewhat similar reactions with iron-salts. A solution of an osmiocyanide, forms with *ferrous* salts a light blue precipitate quickly becoming darker on exposure to the air, and with *ferric* salts a precipitate of a beautiful violet colour. With *cupric* salts, the soluble osmiocyanides form a red-brown precipitate; with *silver*, *mercurous*, and *lead* salts, white crystalline; and with *zinc* and *cadmium* salts, white gelatinous precipitates.

*Osmiocyanide of Barium*,  $\text{Ba}^{\text{I}}\text{Os}^{\text{II}}\text{Cy}^{\text{I}} + 3 \text{ aq.}$  is obtained by treating ferric osmiocyanide with baryta-water—which separates ferric hydrate in the same manner as from ferric ferrocyanide—removing the excess of baryta from the filtrate by carbonic acid, and evaporating over sulphuric acid. It forms small rhombic prisms with basal end-faces, transparent, reddish-yellow, easily soluble in water and in aqueous alcohol. They are permanent in the air at ordinary temperatures, but give off all their water between  $50^{\circ}$  and  $60^{\circ}$  C. (Martius.)

*Osmiocyanide of Barium and Potassium* ( $\text{Ba}^{\text{I}}\text{K}^{\text{I}}\text{Os}^{\text{II}}\text{Cy}^{\text{I}} + 3 \text{ aq.}$  separates from a mixture of the boiling concentrated solutions of 1 pt. chloride of barium and 2 pts. osmiocyanide of potassium, in small light-yellow crystals having the form of acute rhombohedrons with the end-face  $\text{oR}$ . The salt is efflorescent, dissolves sparingly in cold, freely in boiling water. (Martius.)

*Osmiocyanide of Hydrogen*, *Hydro-osmiocyanic acid*, *Osmioprussic acid*,  $\text{H}^{\text{I}}\text{Os}^{\text{II}}\text{Cy}^{\text{I}}$ , is obtained by mixing a cold saturated solution of osmiocyanide of potassium with an equal volume of fuming hydrochloric acid, collecting the precipitated osmioprussic acid on a filter (freed from iron by washing with hydrochloric acid), washing it with strong hydrochloric acid, and crystallising it from alcohol covered with a layer of ether. It forms transparent, colourless, shining, prismatic crystals, belonging to the hexagonal system. They are anhydrous, and permanent in the air when dry, but decompose in the moist state, giving off hydrocyanic acid and leaving proto-cyanide of osmium. The acid dissolves easily in water and in alcohol; and is precipitated therefrom by a small quantity of ether; it has a sour, metallic, astringent taste, a strong acid reaction, and decomposes carbonates. (Martius.)

*Osmiocyanides of Iron.* The *ferrous* salt,  $\text{Fe}^{\text{I}}\text{Os}^{\text{II}}\text{Cy}^{\text{I}}$ , is the light blue precipitate produced by soluble osmiocyanides in ferrous solutions. It quickly becomes darker on exposure to the air, and is converted by nitric acid into a violet compound, probably  $\text{Fe}^{\text{II}}\text{Os}^{\text{II}}\text{Cy}^{\text{I}}$ , analogous to Turnbull's blue. The same compound is said by Martius to be formed by precipitating osmiocyanide of potassium with a ferric salt; but the precipitate thus formed is more probably *ferric osmiocyanide* ( $\text{Fe}^{\text{III}}\text{Os}^{\text{II}}\text{Cy}^{\text{I}}$ ), analogous to ferric ferrocyanide (p. 227), the reaction being



It has a splendid violet colour, and, as a test for ferric salts, is even more delicate than ferrocyanide of potassium; it settles down quickly, and is not decomposed by boiling water. In drying, it shrinks up to a brittle mass having the colour of pinchbeck. By boiling with alkalis, it is decomposed like ferric ferrocyanide, with separation of ferric hydrate. (Martius.)

*Osmiocyanide of Potassium*,  $\text{K}^{\text{I}}\text{Os}^{\text{II}}\text{Cy}^{\text{I}} + 3 \text{ aq.}$  This salt, the analogue of ferrocyanide of potassium, was discovered by Claus. It is most easily obtained by treating osmate of potassium with cyanide of potassium. A solution of 1 pt. osmic acid in a sufficient quantity of strong potash-ley just to give it an alkaline reaction, is mixed with  $1\frac{1}{2}$  pt. cyanide of potassium; the dark liquid is carefully evaporated to dryness; and the residue is calcined at a gentle heat in a covered porcelain crucible. The solution of the unfused but whitened mass in a small quantity of water, deposits the salt, after filtration, in rather large crystalline plates, which may be purified by recrystallisation. Metallic osmium is not attacked by cyanide of potassium; but when gently ignited with ferrocyanide of potassium, it is almost entirely dissolved; the osmiocyanide thus

formed cannot, however, be separated from the ferrocyanide, because the two salts crystallise together in all proportions.

Osmiocyanide of potassium crystallises from water as a yellow silky powder, or in yellow quadratic laminae, isomorphous with the ferrocyanide. It is insoluble in alcohol and ether. The anhydrous salt is white, melts when heated to redness in a close vessel, with evolution of gas and separation of metallic osmium; when further heated in contact with the air, it yields osmic acid. With strong *hydrochloric acid* it first yields osmiocyanide of hydrogen, then gives off hydrocyanic acid and deposits protocyanide of osmium. Treated with *dilute nitric acid*, it gives off a large quantity of gas, and forms a solution containing a nitro-osmio-cyanogen compound not yet examined, perhaps analogous to a nitroferrocyanide (p. 250). Fused with *sulphur* it appears to yield a sulphosmio-cyanogen compound. It does not appear to form an osmium-compound analogous to ferricyanide of potassium (Martius.) For the reactions of osmiocyanide of potassium with metallic solutions, see page 259.

**CYANIDES OF PALLADIUM.** (Berzelius, Pogg. Ann. xiii. 460.—Fehling, Ann. Ch. Pharm. xxxix. 119.—Rammelsberg, Pogg. Ann. xliii. 139.)

*Palladous Cyanide*, PdCy, is obtained as a yellowish-white precipitate on mixing a palladous salt with cyanide of mercury. It dissolves in ammonia, and the solution yields an abundant crop of crystals of cyanide of palladous ammonium, (NH<sup>+</sup>Pd)Cy.

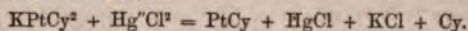
*Potassio-palladous cyanide*, KPdCy<sup>2</sup>, is obtained in rhomboidal crystals by dissolving palladous cyanide in cyanide of potassium, and evaporating.

*Palladic Cyanide*, PdCy<sup>2</sup>.—The compound of palladic chloride with chloride of potassium (see PALLADIUM) stirred up with water and mixed with cyanide of mercury, yields a pale rose-coloured flocculent precipitate which gradually decomposes, giving off hydrocyanic acid. (Berzelius.)

**CYANIDES OF PLATINUM.** (L. Gmelin, *Handbook*, viii. 43.—Döbereiner, Ann. Ch. Pharm. xvii. 250.—Knop, *ibid.* xliii. 111.—Knop and Schnedermann, J. pr. Chem. xxxvii. 461.—Quadrat, Ann. Ch. Pharm. lxiii. 164; lxx. 300.—Gerhardt, Compt. chim. 1850, p. 145; *Traité*, i. 362.—Schafarik, Wien. Akad. Ber. xvii. 57; Gm. x. 506.—Weselsky, J. pr. Chem. lxi. 276; Gm. xii. 499.—Buckton, Chem. Soc. Qu. J. iv. 26.—Hadow, *ibid.* xiii. 106.—C. A. Martius, *Ueber die Cyanverbindungen der Platinmetalle*. Inauguraldissertation, Göttingen, 1860; Ann. Ch. Pharm. cxvii. 357; Jahresber. d. Chem. 1860, p. 230.)

Platinum forms two cyanides, PtCy and PtCy<sup>2</sup>, analogous to the chlorides, and an intermediate compound Pt<sup>2</sup>Cy<sup>3</sup>. The last two are known only in combination; the protocyanide is known in the separate state, but has never been obtained quite pure. It forms a numerous class of double salts, the platino-cyanides MPtCy<sup>2</sup> or MCy.PtCy, which were discovered by L. Gmelin.

*Protocyanide of Platinum*, or *Platinous Cyanide*, PtCy.—This compound is obtained: 1. By calcining mercurous platino-cyanide in a retort at a gentle heat (Döbereiner).—2. By calcining a dried mixture of mercuric chloride and platino-cyanide of potassium, as long as any reaction is apparent, extracting the soluble matters with boiling water, and calcining the residue to free it from mercurous chloride (Knop and Schnedermann):



3. By adding strong sulphuric acid to platino-cyanide of potassium, whereby it becomes heated, and dissolving out the soluble salts with water (Knop and Schnedermann).—4. By heating platino-cyanide of ammonium to about 300° C. (Schafarik).—5. By boiling platino-cyanide of hydrogen with nitric acid. (Schafarik.)

Platinous cyanide, according to the manner in which it is prepared, is greenish-yellow or sulphur-yellow in the recent state, and of a rusty colour when dry. By the fourth method, it is obtained in yellow crystals, which are pseudomorphs of the ammonium-salt. It is insoluble in water, acids, and alkalis, but in the moist state it dissolves in the cyanides of the alkali-metals, yielding platino-cyanides. When heated in the air, it burns away, leaving metallic platinum. Schafarik's product (4), yielding the metal in distinct pseudomorphous crystals. The quantity of metallic platinum thus obtained varies considerably, according to the method by which the compound has been prepared. According to Döbereiner, it yields from 78 to 79 p. c., the formula requiring 79.2 p. c. Quadrat, however, found in the compound prepared by Döbereiner's method, only 71.7 p. c., and in that prepared by Knop and Schnedermann's process, only 72.8 p. c. platinum, numbers agreeing approximately with the formula of sesquicyanide of platinum, Pt<sup>2</sup>Cy<sup>3</sup>, which requires 71.5 p. c. Schafarik, however, found in the products which he obtained by Knop and Schnedermann's method, and likewise by his own methods (4 and 5), from 75.24 to 77.18 p. c. platinum. On the whole, it is

most probable that the products obtained by these several methods consist essentially of protocyanide of platinum, but contaminated with variable quantities of foreign substances which cannot be removed by washing.

*Ammonio-platinous Cyanide*,  $\text{NH}^+\text{PtCy}^-$ . See CYANIDE OF PLATOSAMMONIUM (p. 264).

**Platinocyanides.**  $\text{MPtCy}^2 = \text{MCy.PtCy}$ , or rather  $\text{M}^+\text{Pt}^2\text{Cy}^{4-}$ .—These salts may be regarded as compounds of protocyanide of platinum with a more basic cyanide. Those which are soluble may be obtained by treating protocyanide of platinum with an alkaline cyanide, or the protochloride with excess of an alkaline cyanide, or with an alkaline base and hydrocyanic acid; those which are insoluble are obtained by precipitation. The copper-salt decomposed by sulphydric acid yields platinocyanide of hydrogen, and this, when saturated with bases, likewise yields the several platinocyanides.

The platinocyanides belong to the more stable class of double cyanides (p. 201), exceeding even the ferrocyanides in the force with which they retain the negative metal and disguise it to ordinary tests. Strong nitric and hydrochloric acids, either alone or mixed, extract no platinum from them, even at the boiling heat; they are not decomposed by digestion with mercuric oxide; and strong sulphuric acid at the boiling heat separates the platinum but slowly.

The platinocyanides of the alkali-metals, alkaline-earth-metals, and magnesium, are soluble in water; most of the others are insoluble, or sparingly soluble. The soluble salts crystallise well and are remarkable for the beauty and variety of the colours which the crystals exhibit, whereas the solutions are colourless. The solutions form a smalt-blue precipitate with mercurous salts, white with mercuric salts, and a flocculent blue precipitate with cupric salts.

*Platinocyanide of Ammonium*,  $(\text{NH}^+)\text{PtCy}^-$ .—Obtained by dissolving platinous cyanide (3) in hydrocyanic acid saturated with ammonia (Knop and Schnedermann); by passing dry ammonia-gas over platinocyanide of hydrogen, the latter being kept in excess (Quadrat); by decomposing platinocyanide of potassium with sulphate of ammonium (Quadrat), or by precipitating platinocyanide of barium with a mixture of ammonia and carbonate of ammonium, and slowly evaporating the filtrate (Schafarik). By this last method it is obtained in slender prisms of a deep lemon-yellow colour, exhibiting a splendid blue fluorescence on the surface. These crystals contain 1 at. water ( $\text{NH}^+\text{PtCy}^- + \text{aq.}$ ), and when placed under a bell-jar, together with caustic lime on which ammonia is dropped, they become white and turbid, and give off half their water. These colourless crystals slowly recover their water and turn yellow when exposed to the air. Both the white and the yellow crystals give off the whole of their water at  $160^\circ \text{C.}$ , becoming milk-white and pearly. On dissolving the anhydrous salt in absolute alcohol and evaporating over sulphuric acid, crusts of colourless needles shoot out from the margin of the vessel, and at last coat the entire surface with a network exhibiting a beautiful violet fluorescence; on exposure to the air they rapidly turn yellow. The yellow salt dissolves in about its own weight of water, and in a smaller quantity of alcohol.

*Platinocyanide of Barium*,  $\text{BaPtCy}^2$ .—Prepared: 1. By boiling the copper-salt with caustic baryta, and separating the excess of baryta by a stream of carbonic acid gas (Quadrat).—2. By dissolving platinocyanide of potassium in the smallest possible quantity of water, adding an equivalent quantity of the strongest sulphuric acid (23 pts. acid to 100 pts. potassium-salt), taking care to avoid overheating; then adding 10 vols. alcohol of specific gravity 0.63, mixed with a little ether, and immersing the vessel in cold water, to separate the sulphate of potassium; evaporating the filtrate to one-third; adding water; and saturating it at the boiling heat with carbonate of barium (Schafarik).—3. By triturating 2 pts. protochloride of platinum and 3 pts. carbonate of barium with water, heating the mixture with 10 pts. water nearly to the boiling point, and passing vapour of hydrocyanic acid through the liquid as long as carbonic acid continues to escape.

The salt forms monoclinic crystals, often of considerable size. Ordinary combination  $\infty \text{P.} \infty \text{P} \infty . [\infty \text{P} \infty] . [\text{P} \infty]$ . Inclination of  $\infty \text{P} : \infty \text{P}$  in the clinodiagonal principal section =  $99^\circ 42'$ ;  $[\text{P} \infty] : [\text{P} \infty] = 130^\circ 8'$ . Ratio of axes,  $a : b : c = 2.0861 : 1.8146 : 1$ . Inclination of  $b$  to  $c = 75^\circ 53'$ . The crystals appear green when viewed along the principal axis; sulphur-yellow at right angles to it. Specific gravity = 3.054. They contain 16.3 per cent. water (rather more than 2 at.), which they give off at  $100^\circ \text{C.}$  Easily soluble in hot water. (Quadrat.)

\* This formula is more convenient for expressing the composition of most of the hydrated salts, which, if the smaller formula be used, must be supposed to contain a fractional number of water atoms. The double formula is further recommended by the consideration that the atomic weights of several of the metals, viz. Ba, Sr, Ca, Mg, Mn, Fe, Zn, Pb, and Hg are most probably double of those commonly assigned to them (see CLASSIFICATION, l. 1008, n. 1); thus the formula of platinocyanide of barium is most probably  $\text{BaPt}^2\text{Cy}^{4-}$ , not  $\text{BaPtCy}^2$ , the barred symbol Ba standing for the atomic weight 187.2 double of Ba = 66.6.



*Platinocyanide of Cadmium*,  $\text{CdPtCy}^2$ .—Formed as a crystalline precipitate on mixing platinocyanide of potassium with chloride of cadmium. It is anhydrous, yellowish-white with blue iridescence when dry; when heated it glows and leaves a compound of cadmium and platinum. (Martius.)

*Platinocyanide of Cadmammonium*,  $(\text{NH}^+\text{Cd})^2\text{Pt}^2\text{Cy}^4 + \text{aq.}$ —A solution of the preceding salt in ammonia yields this compound in large white needles, which retain their ammonia somewhat tenaciously. (Martius.)

*Platinocyanide of Calcium*,  $\text{Ca}^2\text{Pt}^2\text{Cy}^4 + 5\text{aq.}$ —Obtained like the barium-salt. Slender needles which exhibit a trichroism similar to that of the barium-salt, appearing lemon-yellow and siskin-green by transmitted, and bluish with a diamond lustre by reflected light. They are very soluble in water, and give off 20.44 per cent. water at  $140^\circ\text{C.}$  (Quadrat.)

*Platinocyanide of Cerium*,  $\text{Ce}^2\text{Pt}^2\text{Cy}^4 + 6\text{aq.}$ —Obtained by mixing cerous sulphate with platinocyanide of barium; evaporating the filtrate at  $100^\circ\text{C.}$ , exhausting the residue with warm alcohol, evaporating again, dissolving in water, and crystallising. Forms fine yellow strongly fluorescent prisms, with azure-blue surface-lustre, and exhibiting a siskin-green tint along the axis. It is permanent in the air, gives off half its water over sulphuric acid, but cannot be completely dehydrated by heat without decomposition. From the alcoholic solution it crystallises in white crystals, which contain less water, but when exposed to the air, or when breathed upon, quickly take up water, and are converted into the yellow salt. (Czudnowicz, J. pr. Chem. lxxx. 16.)

*Platinocyanide of Cobalt-ammonium*,  $(\text{NH}^+\text{Co})\text{PtCy}^2$ .—Obtained as a crystalline flesh-coloured powder by precipitating platinocyanide of potassium with chloride of cobalt, dissolved in a mixture of caustic ammonia and carbonate of ammonia. (Knop and Schnedermann.)

*Platinocyanide of Cinchonine*,  $(\text{C}^{20}\text{H}^{22}\text{N}^2\text{O})\text{PtCy}^2$ .—Easily soluble, colourless needles, obtained by decomposing the barium-salt with sulphate of cinchonine and evaporating. (Martius.)

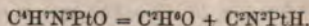
*Platinocyanide of Copper*,  $\text{CuPtCy}^2$ .—Precipitated on adding sulphate of copper to a solution of the potassium-salt (Quadrat). It is a green precipitate, which shrinks very much in drying, forming shining sharp-edged fragments. Gives off cyanogen when heated in close vessels, and leaves a black powder, probably consisting of platinum and oxide of copper (Schafarik). It is insoluble in water and acids, but easily soluble in ammonia, the solution yielding by slow evaporation azure-blue crystals of the following salt. (Quadrat.)

*Platinocyanide of Cuprammonium*,  $(\text{NH}^+\text{Cu})^2\text{Pt}^2\text{Cy}^4 + \text{aq.}$ —Obtained as just described, or by mixing platinocyanide of potassium with nitrate of copper dissolved in ammonia. It then separates after a few hours in dark blue needles containing water of crystallisation. At  $140^\circ\text{C.}$  it gives off ammonia and turns green. (Knop and Schnedermann.)

*Platinocyanide of Ethyl*,  $\text{C}^2\text{H}^5\text{N}^2\text{Pt} + \text{aq.} = (\text{C}^2\text{H}^5)^2\text{PtCy}^2 + \text{aq.} = \text{C}^2\text{H}^5\text{Cy.PtCy} + \text{aq.}$  (C. v. Thann, Ann. Ch. Pharm. cvii. 315.)—Prepared by passing dry hydrochloric acid gas into a solution of hydroplatinocyanic acid in absolute alcohol. The gas is rapidly absorbed, the liquid becomes very hot, and solidifies on cooling to a crystalline pulp, composed of small aurora-red needles. The crystals must be quickly filtered and dried with great care over oil of vitriol and caustic potash.

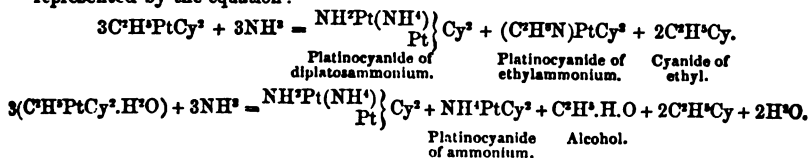
The crystals thus obtained contain 1 at. water, from which they cannot be separated without decomposition. They belong to the trimetric system, and are combinations of a prism with the basic terminal face and a dome. They appear to be isomorphous with platinocyanide of potassium. Under the microscope, the body of the crystal exhibits a brown colour, while the surface varies from azure to dark steel blue.

Hydrated platinocyanide of ethyl is resolved at  $100^\circ\text{C.}$  into alcohol and hydroplatinocyanic acid:

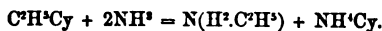


It suffers the same decomposition in contact with water. At higher temperatures it is resolved into platinum cyanide, cyanide of ethyl, and water. Aqueous ammonia added in excess to a concentrated alcoholic solution of platinocyanide of ethyl mixed with four or five times its bulk of ether, forms stellate groups of needles consisting of *platinocyanide of diplatamosammonium* (p. 264); and on evaporating the mother-liquor to dryness, dissolving it in alcohol, and leaving the solution to evaporate over oil of vitriol, it first deposits *hydrated platinocyanide of ammonium*, and then yellow needles

probably consisting of *platinocyanide of ethylammonium*. The decomposition may be represented by the equation:



Probably both these reactions go on together; but the cyanide of ethyl appears to be further acted on by the free ammonia, perhaps yielding ethylamine and cyanide of ammonium:



Dry ammonia gas converts platinocyanide of ethyl into platinocyanide of ammonium and ethylamine:



*Platinocyanide of Ethylammonium*,  $\text{C}^2\text{H}^5\text{N}^3\text{Pt} = (\text{N} \cdot \text{H}^2 \cdot \text{C}^2\text{H}^5)\text{PtCy}^2$ .—The yellow crystals obtained, in the manner above described, by the action of aqueous ammonia on a solution of platinocyanide of ethyl in alcohol and ether, dissolve very readily in water and alcohol; and the solutions evaporated in the air, leave long yellow needles, which, while immersed in the mother-liquor, exhibit a splendid violet iridescence on the surface. (v. Thann.)

*Platinocyanide of Hydrogen. Hydroplatinocyanic acid.*  $\text{HPtCy}^2$ .—Prepared by decomposing the copper-salt suspended in water with sulphydric acid, evaporating the filtrate to dryness, dissolving the residue in a mixture of alcohol and ether, and again evaporating. As thus obtained, it forms hydrated bluish-black prisms, or if the crystallisation has been rapid, greenish-yellow needles with a coppery or golden lustre. They absorb moisture from the air, turning yellow and deliquescent (Quadrat). By decomposing the barium-salt with an equivalent quantity of sulphuric acid, evaporating the filtrate, redissolving in alcohol and ether, and evaporating over sulphuric acid, Wesselsky obtained the acid in crystals 7 or 8 lines long, half a line thick, and having a splendid vermilion colour with blue iridescence on the prismatic faces. These crystals absorbed water from the air, and then assumed the ordinary appearance of hydroplatinocyanic acid.

Hydroplatinocyanic acid turns yellow at  $100^\circ \text{C}$ ., then white, and may be heated to  $140^\circ$  without decomposing. It is soluble in water and in alcohol; the alcoholic solution is colourless. It decomposes carbonates with effervescence. It absorbs ammonia with rapidity, acquiring a yellow colour. Heated with strong sulphuric acid, it is decomposed, yielding hydrocyanic acid and a yellow substance, probably platinous cyanide (Quadrat). Nitric acid decomposes it, with separation of platinous cyanide. (Schafarik.)

*Platinocyanide of Lanthanum*,  $\text{La}^3\text{Pt}^2\text{Cy}^4 + 6 \text{ aq.}$ —Prepared in the same manner as the cerium-salt (p. 262). Crystallises from the aqueous solution in shining rhombic prisms terminated by a brachydiagonal dome. They exhibit dichroism, being yellow inclining to orange by transmitted light, but having a blue surface lustre. When placed over sulphuric acid they give off 3 at. water and acquire a scarlet colour; in vacuo they give off 5 at. water and acquire a dirty yellow-brown colour. From solution in strong alcohol the salt crystallises with difficulty in colourless crystals, which contain less water, but quickly take up an additional quantity and turn yellow. (Czudnowicz, J. pr. Chem. lxxx. 31.)

*Platinocyanide of Lead*,  $\text{PbPtCy}^2$ .—Yellowish-white crystalline powder obtained by precipitation. When heated it behaves like the cadmium-salt. It is soluble in warm dilute nitric acid, solidifies on cooling to a red crystalline magma of platino-sesquicyanide of lead,  $2\text{Pb}^2\text{Pt}^2\text{Cy}^4 + 5 \text{ aq.}$

*Platinocyanide of Magnesium*,  $\text{Mg}^2\text{Pt}^2\text{Cy}^4$ .—Prepared by mixing a solution of the barium-salt with sulphate of magnesium, evaporating the filtrate to dryness, digesting the residue in ether-alcohol, and leaving the solution to evaporate; or by mixing the solution of the potassium-salt with sulphate of magnesium, evaporating to a dry powder, digesting with ether-alcohol, and evaporating (Quadrat). It is thus obtained in fine large square-based prisms, often grouped in rosettes, of a deep red colour by transmitted light; when viewed by reflected light the sides of the prisms exhibit a brilliant beetle-green, and their extremities a deep blue or purple colour. The red crystals contain  $\text{Mg}^2\text{Pt}^2\text{Cy}^4 + 7 \text{ aq.}$  Between  $50^\circ$  and  $40^\circ \text{C}$ . ( $86^\circ$  and  $113^\circ \text{F.}$ ) they give up 1 at. water, and are reduced to  $\text{Mg}^2\text{Pt}^2\text{Cy}^4 + 6 \text{ aq.}$ , which has a bright



yellow colour; this hydrate is likewise deposited from solution at the temperature of 160° F.; also, according to Weselsky, by leaving a solution of the ordinary red and green salt in water, or in absolute alcohol, to crystallise over sulphuric acid. At 212° F. the salt becomes quite white, and then consists of  $\text{Mg}^2\text{Pt}^2\text{Cy}^4 + 2 \text{ aq.}$ , and between 300° and 400° F. it gives off the rest of its water and again becomes yellow. If a portion of this yellow anhydrous salt be laid on the red salt in powder, it will soon abstract water from the latter, and a white layer will be formed between two yellow borders, one consisting of the anhydrous, the other of the 6-hydrated salt (Schafarik; Hadow). The salt is very soluble in water, and forms a nearly colourless solution.

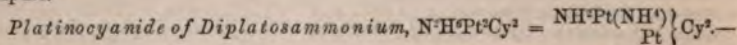
*Platinocyanide of Magnesium and Potassium*,  $(\text{MgK})\text{Pt}^2\text{Cy}^4 + 7 \text{ aq.}$ —Hadow obtained this salt on one occasion, simultaneously with the magnesium salt, by evaporating to dryness a mixture of the solutions of sulphate of magnesium and platinocyanide of potassium, and digesting the residue in weak alcohol (instead of ether-alcohol). The crystals are of a paler red than the preceding, and exhibit a steel-blue lustre by reflected light. Part of the water of crystallisation is given off at 100° C., the rest at a higher temperature. The salt cannot be recrystallised, except from excess of platinocyanide of magnesium, and even then, sudden cooling or agitation of the saturated solution will cause it to separate into its component salts. (Hadow.)

*Platinocyanides of Mercury*.—The mercuric salt,  $\text{Hg}^2\text{Pt}^2\text{Cy}^4$ , is a white precipitate obtained by mixing the solutions of platinocyanide of potassium and mercuric chloride. (Gmelin.)

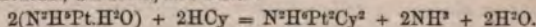
With mercurous nitrate, platinocyanide of potassium forms a blue precipitate, consisting, according to Rammelsberg's analysis, of  $5\text{Hg}^2\text{Pt}^2\text{Cy}^4 \cdot 2\text{HgNO}_3 + 10 \text{ aq.}$  This compound is not soluble in cold water acidulated with nitric acid, and cannot be freed from mercurous nitrate by washing. When boiled with water, the blue colour changes through green and yellow to white, being ultimately converted into mercuric platinocyanide, the liquid containing mercurous nitrate. It is likewise reduced to mercuric platinocyanide by heating it in the state of powder to 200°–250° C. (Döbereiner; Schafarik.) This blue compound is also formed on adding mercuric platinocyanide to mercurous nitrate. (Döbereiner.)

*Platinocyanide of Nickelammonium* ( $\text{NH}^3\text{Ni}$ )  $\text{PtCy}^2$ , produced by adding the potassium-salt to an ammoniacal solution of nitrate of nickel, forms violet needles which yield a pale violet crystalline powder.

*Platinocyanide of Platinum*  $\text{Pt}^2\text{Cy}^4 = \text{ptPtCy}^2$ . [ $\text{pt} = \frac{1}{2}\text{Pt} = 49.5$ ].—This, according to Gerhardt (*Traité* i. 366), is the rational constitution of the yellow compound, commonly called protocyanide of platinum (p. 260). But, as already observed, it is most probable that this compound is essentially the protocyanide more or less impure.



Precipitated on adding platinocyanide of potassium to a solution of chloride of diplatosammonium (ammonio-protochloride of platinum: see PLATINUM);—also on adding cyanide of potassium to chloride of diplatosammonium; also when cyanogen gas is passed into a solution of hydrate of diplatosammonium, the reaction depending on the decomposition of water, the elements of which unite with the cyanogen, forming hydrocyanic and cyanic acids, and the hydrocyanic acid forming platinocyanide of diplatosammonium, ammonia, and water:



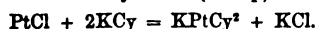
It is a white crystalline precipitate, nearly insoluble in cold water, but may be crystallised from boiling water, and is then deposited in microscopic hexagonal tables often grouped in stars. Heated in the air, it takes fire and burns like amadou. It dissolves, without decomposition, in potash and in ammonia, also in dilute acids, but is decomposed by strong nitric and sulphuric acids. With nitrate of silver it forms a precipitate of platinocyanide of silver, while nitrate of diplatosammonium remains in solution. (Buckton.)

*Cyanide of Platosammonium*,  $\text{NH}^3\text{PtCy}$ , a compound isomeric with the preceding, is obtained by digesting chloride of platosammonium with cyanide of silver. The decanted liquid is yellow, and yields, by concentration, slender needles of a pale yellow colour, much more soluble in water and ammonia than the platinocyanide of diplatosammonium. (Buckton.)

*Platinocyanide of Potassium*,  $\text{KPtCy}^2 = \text{KCy} \cdot \text{PtCy}$ .—This salt, discovered by Leopold Gmelin, is produced by fusing cyanide or ferrocyanide of potassium with platinum: hence platinum crucibles are strongly attacked by alkaline cyanides in a state of fusion.



**Preparation.** 1. A mixture of equal parts of spongy platinum and ferrocyanide of potassium is heated nearly to redness in a glass or crucible (if the heat applied be insufficient, the ferrocyanide of potassium remains undecomposed, and if it be too great, the platinum-salt is decomposed); the mass is dissolved in water; the filtrate evaporated at a gentle heat; the warm liquid separated by decantation from any crystals of undecomposed ferrocyanide of potassium that may have been formed, then left to cool till the platinum-salt is crystallises; and this salt is purified by pressure between paper and recrystallisation, both from ferrocyanide and from cyanide of potassium (Gmelin).—2. Dichloride of platinum is converted by heat into protochloride; an aqueous solution of cyanide of potassium is completely saturated with the latter; and the filtrate is evaporated and left to crystallise (Knop):



Since a large quantity of platinum-salt remains dissolved in the mother-liquor, which contains the chloride of potassium, it must be evaporated and mixed with sulphuric acid: hydrochloric acid is then evolved, and a yellow gummy precipitate formed, consisting of protocyanide of platinum, which separates almost completely on boiling the liquid with excess of sulphuric acid. The liquid is then diluted with water; the precipitate is thrown on a filter, washed with water, and dissolved while hot in aqueous cyanide of potassium; and the liquid is boiled till the evolution of ammonia (from the cyanate of potassium) ceases, and then brought to the crystallising point. (Knop and Schnedermann).—3. A concentrated solution of dichloride of platinum is added to the aqueous solution of cyanide of potassium, and the mixture is heated till the precipitate consisting of chloroplatinate and the chloroplatinate of potassium is redissolved, then left to crystallise.—4. Chloroplatinate of ammonium stirred up with water containing lumps of caustic potash, is dissolved at 100° C. in a strong aqueous solution of cyanide of potassium; the solution is boiled till it no longer gives off ammonia; and the filtrate is left to crystallise. In this manner the salt is obtained quite pure in needles 2 or 2½ inches long, and a line in thickness. The addition of caustic potash prevents the formation of cyanide of ammonium, and of the double platinocyanide of ammonium and potassium. (Martius.)

**Properties.**—Platinocyanide of potassium forms long rhombic prisms, yellow by transmitted and blue by reflected light. The dominant faces are P and ∞P. Inclination of ∞P: ∞P = 97°; P: ∞P = 122°. The crystals contain water, their formula being  $\text{KPtCy}^2 + \frac{3}{2}\text{aq.}$  or rather  $\text{K}^2\text{Pt}^2\text{Cy}^4 + 3\text{aq.}$  They effloresce rapidly in the air, becoming opaque and rose-coloured; at 100° C. they give off 12.4 p. c. of water, assuming first a white and then an orange-yellow colour. At a higher temperature, the residue gives off 0.22 p. c. more water (12.62 p. c. in all), again becoming white, and ultimately fusing into a grey and yellow mass, which is very apt to run over the sides of the vessel (Gmelin). The dry salt heated out of contact with the air does not decompose at any temperature between 400° and 600° C. (Knop and Schnedermann). Nitric acid decomposes the salt, forming nitre and a transparent and colourless jelly. Mixed with an equal weight of strong sulphuric acid and with water, and evaporated, it forms a yellow tenacious mass. Dilute sulphuric acid colours it orange-yellow (Gmelin).—It dissolves in strong sulphuric acid without evolution of hydrocyanic acid; the solution heated to the boiling point yields protocyanide of platinum in thick yellow flakes, no hydrocyanic acid escaping, but a gas which burns with a blue flame, probably carbonic oxide. If the quantity of water added to the sulphuric acid solution is just sufficient to produce intense heat, the cyanide of platinum still separates out; but if too much water be added, it does not. (Knop and Schnedermann.) Boiled for some time in aqueous solution with chlorate or chromate of potassium, it is converted into platinidcyanide of potassium. The same effect is produced by peroxide of lead, with formation of carbonate of potassium and carbonate of lead. Chlorine, bromine, and iodine first convert it into platinidcyanide, and afterwards into a compound of that salt with chloride, bromide, or iodide of potassium (Martius.) According to Hadow, the compounds thus formed consist of 5 at. platinocyanide with 1 at. Cl. Br., &c. (p. 266).

Platinocyanide of potassium dissolves abundantly in warm water, but a considerable portion separates out on cooling.

Quadrat (Ann. Ch. Pharm. lxi. 167) by adding protochloride of platinum to an aqueous solution of cyanide of potassium, and evaporating the filtrate to the crystallising point, obtained well-defined yellow crystals which he found by analysis to agree with the formula  $\text{K}^2\text{Pt}^2\text{Cy}^4 + \frac{21}{2}\text{aq.}$ , or  $\text{KCy}.6\text{KPtCy}^2 + \frac{21}{2}\text{aq.}$ , and from this salt he obtained, by double decomposition, a number of others said to be of similar constitution, and therefore represented by the general formula  $\text{M}^2\text{Pt}^2\text{Cy}^4$ , or  $\text{MCy}.6\text{MPtCy}^2$ . These salts Quadrat designates as platino-platinidcyanides. The potassium-salt

prepared by Quadrat's method has, however, been analysed by Gerhardt, Laurent, and Schafarik, who all agree in assigning to it, not the formula given by Quadrat, but the formula of platinocyanide of potassium,  $\text{KPtCy}^2$ . Hence it would appear that Quadrat's platino-platinidcyanides were merely platinocyanides not quite pure.

Platinocyanide of potassium, mixed in solution with other soluble platinocyanides, yields crystalline double salts of analogous composition, and of much brighter and deeper colour than the component salt. *Platinocyanide of potassium and sodium*  $(\text{KNa})\text{Pt}^2\text{Cy}^4 + 6 \text{ aq.}$ , prepared as above or by decomposing platinocyanide of copper with a solution of the carbonates of potassium and sodium, forms monoclinic crystals  $(\infty \text{P} \cdot [\infty \text{P}\infty] \cdot [\text{P}\infty])$  of a bright orange colour by transmitted, and steel-blue by reflected light, with siskin-green fluorescence. The salt  $(\text{K}^2\text{Sr})\text{Pt}^2\text{Cy}^4$  forms monoclinic crystals, with yellow body-colour and blue iridescence on the surface. The salts  $(\text{KCa})\text{Pt}^2\text{Cy}^4$  and  $(\text{K}^2\text{Ba})\text{Pt}^2\text{Cy}^4$  exhibit a fine deep gold colour. (Martius.)

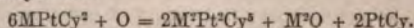
*Platinocyanide of Silver* is a white precipitate, resembling cyanide of silver.—*Platinocyanide of argent-ammonium*  $(\text{NH}^3\text{Ag})\text{PtCy}^2$  is obtained by dissolving carbonate of silver in ammonia, and adding a solution of platinocyanide, or platinosesciquianide of potassium. It forms colourless or slightly flesh-coloured needles, insoluble in pure water, but soluble at the boiling heat in strongly ammoniacal water. An ammoniacal solution of nitrate of silver mixed with ammonia yields, after a few hours, needles which appear to be hydrated. (Knop and Schnedermann.)

*Platinocyanide of Sodium*,  $\text{NaPtCy}^2 + x \text{ aq.}$ , obtained by boiling the copper-salt with carbonate of sodium, forms large crystals belonging to the monoclinic system.

*Platinocyanide of Strontium*,  $\text{Sr}^2\text{Pt}^2\text{Cy}^4 + 5 \text{ aq.}$ , prepared by saturating hydro-platinocyanic acid with carbonate of strontium, or by decomposing the copper-salt with strontia-water, forms sometimes milk-white, sometimes transparent crystals, which, when exposed to the air, acquire a violet tint throughout. When left over sulphuric acid for twenty-four hours, they acquire a splendid purple colour, like that of a solution of permanganate of potassium, and a gold-green metallic surface-lustre, but on exposure to the air for a few days, they completely regain their previous appearance. At  $100^\circ \text{C}.$ , the salt becomes turbid throughout, and acquires a deep orange colour, deeper than that of the dry barium-salt, the gold-green surface-lustre being at the same time changed to azure. At  $150^\circ \text{C}.$  the salt becomes white and anhydrous, but is so sensitive to moisture, that when breathed upon, it immediately acquires a blackish-purple colour. (Schafarik.)

*Platinocyanide of Zinc-ammonium*,  $(\text{NH}^3\text{Zn})\text{PtCy}^2$ , is obtained in large colourless crystals by adding platinocyanide of potassium to an ammoniacal solution of chloride of zinc.

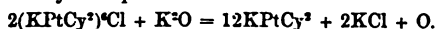
**Platinidcyanides.** *Platinosesciquianides.*  $\text{M}^2\text{Pt}^2\text{Cy}^4 = 2\text{M}^2\text{Cy} \cdot \text{Pt}^2\text{Cy}^2$ .—These salts are produced by the action of nitric acid, chlorine, bromine, and other oxidising agents on the platinocyanides:



They have a peculiar coppery lustre, and are all soluble in water and alcohol, forming colourless solutions, excepting the lithium-salt, the solution of which is yellowish (Weselsky). They give off cyanogen when heated, leaving a residue of platinocyanide. Like the ferricyanides, they separate iodine from iodide of potassium, and exert a bleaching action in presence of alkalis. (Hadow.)

According to Hadow (Chem. Soc. Qu. J. xiii. 106), the composition of the platinidcyanides is not correctly represented by the formula above given. For, as the proportion between the platinum and the basic metal is the same in this formula as in that of the platinocyanides, it is not easy to see how the platinidcyanides are produced from the platinocyanides by oxidation. Weselsky's equation supposes that platinum is removed at the same time as the basic metal; but this is regarded by Hadow as inconsistent with the known stability of the platinocyanides. Moreover, when platinidcyanides are reduced to platinocyanides by the action of potash, no cyanide of potassium appears to be formed. Hadow concludes, from his own analyses of the platinidcyanides, that they are merely platinocyanides combined with a certain quantity of chlorine, bromine, nitryl, &c., according to the oxidising agent used in their formation, and accordingly divides them into *chloroplatinocyanides*, *bromoplatinocyanides*, &c. The compound  $\text{PtCy}^2 \cdot \text{KCl}$  (p. 267) he regards as a *perchloroplatinocyanide of potassium*,  $\text{KPtCy}^2 \cdot \text{Cl}$ , in which the platinocyanide is combined with the maximum quantity of chlorine that it is capable of taking up. Moreover as 6 at. of platinocyanide of potassium  $(\text{KPtCy}^2)^4$ , require 6 at. chlorine to convert them into the perchlorocyanide, whereas, according to Hadow, the chloroplatinocyanide requires only 5 at. chlorine to produce the same compound, he concludes that the formula of the chloroplatinocyanide is  $(\text{KPtCy}^2)^4 \cdot \text{Cl}$ . On this view

the oxidising action of the salt in presence of potash, without formation of cyanide of potassium is explained by the equation:



The chloroplatinocyanides may also be regarded as compounds of platinocyanides and perchloroplatinocyanides:



And, in fact, on mixing the concentrated solutions of the platinocyanide and perchloroplatinocyanide, the copper-coloured needles of the chloroplatinocyanide immediately separate out. On the other hand, on mixing the solution of chloroplatinocyanide of potassium with a zinc-salt, platinocyanide of zinc is precipitated, and perchloroplatinocyanide of potassium remains in solution.

The corresponding bromine-, nitro-, &c., compounds are similarly constituted with Br, NO<sup>2</sup>, &c. in place of Cl. No iodine-compounds of the class appear to exist, but an *oxysulphoplatinocyanide of potassium*,  $(\text{KPtCy}^2)_2\text{SO}_4$ , is obtained as a copper-red mass, with moss-like ramifications, on adding peroxide of lead to a solution of platinocyanide of potassium acidulated with sulphuric acid.

The perchloroplatinocyanides give with *mercurous nitrate* a white, and with *cupric salts* a finely pulverulent blue precipitate, whereas the platinocyanides give with *mercurous nitrate* a small-blue, and with *cupric salts* a flocculent blue precipitate. The perchloroplatinocyanides separate iodine from metallic iodides, and when immersed in a solution of platinocyanide of potassium immediately become covered with copper-red needles. The chloro- (or bromo-, nitro-, &c.) platinocyanides exhibit the reactions of the two salts of which they may be made up.

As Hadow's results differ from those of all other chemists who have examined the so-called platinidcyanides, the composition of these salts must for the present be considered doubtful.

*Platinidcyanide of Ammonium*,  $(\text{NH}_4)\text{Pt}^2\text{Cy}^3$ , crystallises in needles containing  $\frac{1}{2}$  at. water (Knop and Schnedermann). They have a golden yellow metallic lustre, become steel-grey at 160° C. with partial decomposition, and lemon-yellow between 180° and 190°. (Weselsky.)

*Platinidcyanide of Lead*,  $2\text{Pb}^2\text{Pt}^2\text{Cy}^3 + 5\text{aq.}$ —This salt crystallises on cooling from a solution of platinocyanide of lead in warm dilute nitric acid. It may be obtained pure by gradually adding nitric acid of specific gravity 1.2 to a mixture of the concentrated solutions of platinocyanide of potassium and acetate of lead, and leaving the mixture to cool. It then often separates in needle-shaped crystals 2 inches long, having a light red-lead colour in the body, and deep azure-blue on the surface. At 40° C. they give off 1 at. water, and assume a vermilion colour; between 50° and 60° they become cherry-red, at a stronger heat flesh-red; and at 200°, perfectly white and anhydrous. (C. F. Martius.)

*Platinidcyanide of Lithium*,  $\text{Li}^2\text{Pt}^2\text{Cy}^3 + 3\text{aq.}$ , is very soluble in water and alcohol. (Weselsky.)

*Platinidcyanide of Magnesium* forms a blackish violet satiny mass of microscopic needles. (Weselsky.)

*Platinidcyanide of Potassium*,  $\text{K}^2\text{Pt}^2\text{Cy}^3 + 3\text{aq.}$ —Obtained by passing chlorine into a warm solution of platinocyanide of potassium, sufficiently concentrated to deposit crystals on cooling, till small copper-red needles begin to form in it and ultimately convert the liquid into a thick pulp. The passage of the gas is then discontinued, the mass is thrown on a filter and slightly pressed, to facilitate the removal of the mother-liquor, and then subjected to strong pressure between folds of filtering paper. It is purified by recrystallising it several times from the smallest possible quantity of boiling water, slightly acidulated with hydrochloric acid to saturate any cyanate or carbonate of potassium that may be mixed with the salt, and would reduce it to platinocyanide when heated. (Knop.)

Platinidcyanide of potassium crystallises in beautiful prisms, green by transmitted, and having a coppery metallic lustre by reflected light. Viewed in the mass, it resembles a tissue composed of fine needles of copper. It dissolves easily in water, but is insoluble in alcohol. The solution forms a white precipitate with mercuric salts, deep blue with mercurous salts, greenish blue with cupric salts. (Knop.)

The salt is easily decomposed by heat, giving off cyanogen, then acquiring a brownish-yellow colour, and ultimately melting to a brown mass (Knop). According to Weselsky, it turns dark green at 180° C., and yellow at 200°, without losing its metallic lustre. When left over sulphuric acid in vacuo, it gives off part of its water, turns black, and is afterwards only partially soluble in water. By digestion with potash it is reduced to platinocyanide. Strong sulphuric acid decomposes it, with separation of a yellowish powder, which gives off cyanogen at a red heat, and leaves a



residue containing platinum and potassium. When digested with cold concentrated hydrochloric acid, it first turns orange-yellow and then white, but resumes its copper colour when heated. (Knop.)

Hadow, as already observed, regards this salt as platinoeyanide of potassium united with  $\frac{1}{2}$  at. Cl, Br, NO<sup>2</sup>, &c., according to the oxidising agent used in its formation, that is to say, as (KPtCy<sup>2</sup>)<sup>2</sup>Cl, (KPtCy<sup>2</sup>)<sup>2</sup>Br, &c., or as a compound of chloroplatinoeyanide, &c., with perchloroplatinoeyanide, &c. (p. 267). He gives as the easiest method of preparing the chlorine or bromine compound, to treat  $\frac{1}{2}$  of a concentrated solution of platinoeyanide of potassium with excess of chlorine or bromine, and after gently warming it, add to it the remaining  $\frac{1}{2}$  of the platinoeyanide: the pure salt then separates out after a short time. The crystals of *chloroplatinoeyanide of potassium* contain K<sup>2</sup>Pt<sup>2</sup>Cy<sup>2</sup>Cl +  $\frac{3}{2}$ H<sup>2</sup>O, of which 9 at. go off at 100° C., the rest at 186° (Hadow.)

*Compound of Platine Cyanide with Chloride of Potassium*, PtCy<sup>2</sup>.KCl + aq.; according to Hadow, *Perchloroeyanide of Potassium*, KPtCy<sup>2</sup>.Cl + aq.—Obtained by dissolving platinoeyanide of potassium in nitromuriatic acid heated nearly to boiling (Knop and Schnedermann), or by adding permanganate of potassium to a solution of the same salt acidulated with hydrochloric acid (Hadow), and evaporating at the heat of the water-bath. The liquid on cooling deposits the salt in large rhomboidal plates belonging to the triclinic system, very soluble in water and in alcohol, while the mother-liquor retains chloride of potassium.

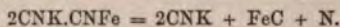
The salt is very efflorescent. When heated it gives off cyanogen, and if calcined at a gentle heat, leaves a residue of platinoeyanide and chloride of potassium; but if more strongly heated, leaves metallic platinum and chloride of potassium. When sulphurous acid gas is passed into the solution and the liquid is then left to evaporate, it deposits crystals of platinoeyanide of potassium mixed with platinoeyanide. A similar reduction is effected by zinc and by ammonia. (Knop and Schnedermann.)

**CYANIDE OF PHOSPHORUS.** See page 255.

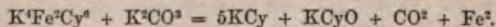
**CYANIDE OF POTASSIUM.** CNK = KCy. This salt is produced by the direct combination of cyanogen and potassium. The metal absorbs cyanogen slowly at ordinary temperature, but when heated, it quickly takes up a volume of the gas equal to the volume of hydrogen which the same quantity of potassium would eliminate from water. Potassium heated in the vapour of hydrocyanic acid is also converted into cyanide, with separation of a quantity of hydrogen equal to that which it would eliminate from water.

The formation of cyanide of potassium by fusing azotised organic matters with carbonate of potassium, by igniting nitrates or nitrites with organic substances, and by passing nitrogen gas or atmospheric air over an ignited mixture of charcoal and carbonate of potassium, has been already mentioned (pp. 198, 238).

*Preparation.*—Cyanide of potassium is prepared by igniting the ferrocyanide (yellow prussiate) either alone or mixed with carbonate of potassium. The former method, when properly conducted, yields a pure product, the ferrocyanide being resolved by heat into cyanide of potassium, carbide of iron, and nitrogen:



One-third of the cyanogen is, however, resolved into carbon and nitrogen, so that only two-thirds is obtained in the form of cyanide of potassium. The latter method yields a larger product, five-sixths of the cyanogen remaining as cyanide of potassium, but the salt thus obtained is mixed with cyanate and carbonate of potassium:



The presence of these impurities does not, however, interfere with many of the purposes to which cyanide of potassium is applied: hence the process is frequently used.

1. *By simple ignition of the ferrocyanide.* Crystallised yellow prussiate is dehydrated by heating it on an iron plate till it forms a dirty white mass on cooling. It is then pulverised, pressed into an iron crucible, and the crucible with its cover on is subjected to a moderate red heat, till a sample of the fused mass taken out on a glass rod, appears white and exhibits the aspect of porcelain on cooling. The crucible is then taken out of the fire, left at rest till the carbide of iron has settled down to the bottom, and the fused cyanide of potassium is poured out on a marble slab or a plate of polished metal. Care must be taken not to apply too strong a heat, which would partly decompose the cyanide into nitrogen and carbide of potassium, and not to leave the fused mass too long in contact with the carbide of iron, as a certain quantity of ferrocyanide may then be reproduced. (Robiquet, J. Pharm. [3] xvii. 643; Geiger, Ann. Ch. Pharm. i. 44.)

2. *By igniting the ferrocyanide with carbonate of potassium.* An intimate mixture

of 8 pts. anhydrous ferrocyanide and 3 pts. carbonate of potassium (the proportion indicated by the equation above given), is introduced by small portions into a cast-iron crucible previously heated to low redness. After all the material has been added, the crucible is kept in the fire till the melted mass exhibits on cooling the aspect of porcelain, as above mentioned; it is then taken out, left at rest till the metallic iron produced by the decomposition has settled down, and the fused salt is poured out; or it is left to cool, and dissolved out by water or alcohol (F. and E. Rodgers, Phil. Mag. [3] iv. 93.—Liebig, Ann. Ch. Pharm. xli. 285).—The carbonate of potassium used in this preparation must be free from sulphate, which would be reduced by the cyanide to sulphide. An iron crucible is preferable to an earthen one, because the latter is penetrated by the fused salt, and imparts silica to it. (Haidlen and Fresenius, Ann. Ch. Pharm. xliii. 130.)

3. Cyanide of potassium may also be prepared by igniting in a covered crucible a mixture of 10 pts. prussian blue and 13 pts. carbonate of potassium, and exhausting the cooled mass with water or alcohol. Also by throwing cyanide of mercury on carbonate of potassium heated nearly to redness. (F. and E. Rodgers.)

4. The attempts to prepare cyanide of potassium on the manufacturing scale by means of atmospheric nitrogen, have already been described. The salt is often produced in considerable quantity in the blast-furnaces in which iron ores are smelted with coal or coke; hence Bunsen has suggested the construction of a blast-furnace expressly for the production of cyanide of potassium, the furnace being filled with coke or charcoal and potash in alternate layers, the whole intensely heated under the influence of a strong blast, and the cyanide running down into a receiver at the bottom. (*Reports of the British Association*, 1845, p. 185.)

*Properties.*—Cyanide of potassium crystallises in transparent colourless cubes or forms derived therefrom. It is inodorous when dry, but when exposed to the air in the moist state, it is decomposed by the carbonic acid of the air, and exhales the odour of prussic acid. Its taste is acrid and caustic, somewhat like that of bitter almonds. It is very fusible, melting at a dull red heat to a transparent liquid, which, on cooling, solidifies to a dull opaque mass having the aspect of porcelain. At a white heat it appears to volatilise without decomposition. It has an alkaline reaction, and is intensely poisonous.

Cyanide of potassium is easily soluble in *water* and very deliquescent, so that it must always be kept in tightly closed vessels. It likewise dissolves readily in *hydrated alcohol*, but is insoluble in *absolute alcohol*.

*Decompositions.*—1. The aqueous solution of cyanide of potassium may be kept unaltered in closed vessels at ordinary temperatures, but when boiled, it is resolved into ammonia and formate of potassium:



The cyanide heated with *hydrate of potassium* likewise yields ammonia and formate of potassium, at first; but the latter compound is resolved, before the heat rises to redness, into hydrogen and carbonate of potassium (Pelouze).—Hence, as Gay-Lussac long ago observed (Ann. Ch. Phys. viii. 440), ammonia is likewise evolved when hot cyanide of potassium is dissolved in water, or cold cyanide of potassium in hot water.

2. When the solution is boiled down in contact with the *air*, hydrocyanic acid is evolved, and there remains more carbonate than formate of potassium. When moist or dissolved cyanide of potassium is exposed to the air at ordinary temperatures, it gradually absorbs carbonic acid, gives off hydrocyanic acid, and is converted into carbonate.

3. Cyanide of potassium detonates violently when heated with *nitrate* or *chlorate* of potassium.

4. Cyanide of potassium under various circumstances takes up 1 at. *oxygen*, and is thereby converted into cyanate. This effect takes place, though very slowly, when the cyanide is fused in contact with the air; more quickly when it is fused with peroxide of manganese, arsenic, antimony, lead, or with the oxides of tin, iron, or copper—in the last case with ignition. The peroxide of manganese is thereby reduced to protoxide, and the other oxides to the metallic state. (Liebig, Ann. Ch. Pharm. xli. 289.)

5. Cyanide of potassium fused with *sulphate of potassium*, yields cyanate and sulphide of potassium (Liebig).—Cyanide of potassium may likewise exert a reducing action in the moist way; thus, from aqueous *alloxan*, after a few hours, it throws down dialurate of potassium. (Liebig.)

6. Cyanide of potassium, fused with *sulphur*, is converted into sulphocyanate (Porrett), and similarly when heated with sulphide of antimony or sulphide of tin, the fused metal separating out (Liebig).—Sulphur does not dissolve in aqueous cyanide of potassium, but *selenium* dissolves readily, even at ordinary temperatures. (Wiggers, Ann. Ch. Pharm. xxix. 319.)



7. Cyanide of potassium boiled with *iodine* takes up a large quantity of that substance, forming first a brown and afterwards a colourless liquid, which solidifies on cooling, and forms a crystalline magma of iodide of cyanogen (Liebig, *Ann. Ch. Pharm.* 1. 355). Probably in this manner:  $KCy + I^2 = KI + CyI$ . According to Langlois (*Ann. Ch. Phys.* [3] lx. 220), the crystals consist of a compound of cyanide of potassium with iodide of cyanogen. (See CYANOGEN, IODIDE OF.)

8. Cyanide of potassium takes up *iodide of nitrogen* without any evolution of gas; the colourless solution evaporated in *vacuo*, yields a crystallo-granular, very deliquescent mass, the solution of which smells of iodoform, and produces a yellow precipitate with corrosive sublimate. (Millon, *Ann. Ch. Phys.* [2] lxi. 78.)

Cyanide of potassium forms numerous compounds with other metallic cyanides, the description of which is given with those cyanides.

*Uses.*—Cyanide of potassium is of great use to the experimental chemist, both for its reducing and its solvent powers. As a reducing agent, it is nearly equal in power to potassium itself, and is especially useful in blowpipe reactions. As a solvent, it is much used in analysis for separating metals one from the other, *e.g.* cobalt from nickel (i. 1047), copper from bismuth, cadmium, &c. (p. 62);—also in various processes of volumetric analysis, the estimation of copper, for example (p. 48). It is used in medicine for the same purpose as prussic acid; and by photographers for fixing proofs on moist collodion, and for removing stains of nitrate of silver from the hands, which it does by forming a soluble double cyanide of silver and potassium. This last mode of employing it is, however, very dangerous, as if it comes in contact with a cut or scratched surface, it is apt to produce painful and troublesome sores, and may even give rise to dangerous symptoms of poisoning. The removal of silver stains may be quite as well effected by means of a solution of iodine in iodide of potassium. (See a paper by M. Davanne, *Répertoire de Chimie appliquée*, May 1861, p. 182.)

Cyanide of potassium is extensively used in galvanic gilding and silvering, indeed, the chief consumption of it is for this purpose.

*Testing and Valuation.*—Commercial cyanide of potassium may contain the following impurities: *Carbonate of Potassium*. This salt remains behind when the cyanide is dissolved in hot alcohol of 36° Bm.—*Chloride*. The salt ignited with 2 pts. of nitre and 10 pts. carbonate of potassium (both free from chloride), then dissolved in water and super-saturated with nitric acid, precipitates nitrate of silver.—*Cyanate*. Contained in the cyanide prepared by Rodgers' process, and separates from the hot solution in laminae. If the portion of the cyanide which is soluble in alcohol of 36° Bm. gives off carbonic acid on addition of acids, and forms a precipitate of carbonate with barium-salts, the presence of cyanate may be inferred (p. 192).—*Ferrocyanide*. Precipitate of prussian blue with a ferric salt (which must be quite free from ferrous salt), after saturation with hydrochloric acid. With sulphate of copper, a precipitate which, on addition of hydrochloric acid, does not turn white, but red.—*Formate*. The salt blackens on ignition. Also on expelling the hydrocyanic acid from the solution by a stream of carbonic acid, evaporating to dryness, exhausting with alcohol, again evaporating and distilling the residue with dilute sulphuric acid, formic acid passes over, and may be recognised by its power of reducing silver and mercury-salts.—*Silicate*. Residue of silica, after supersaturation with hydrochloric acid, evaporation to dryness, and digestion in water.—*Sulphate*. Precipitate with barium-salts after supersaturation with hydrochloric acid.—*Sulphide*. Dirty precipitate with lead-salts.

The proportion of pure cyanide of potassium in a given sample may be estimated by means of a standard solution of nitrate of silver. Since 1 at. cyanide of potassium is required to precipitate 1 at. silver, and 1 at. more cyanide of potassium to redissolve the precipitate as cyanide of silver and potassium,  $KAgCy^2$ , it follows that 1 at. silver precipitated and redissolved corresponds to 2 at. cyanide; or 108 pts. to  $2 \times 65 = 130$  pts. cyanide of potassium. (Glassford and Napier, *Phil. Mag.* [3] xxv. 58.)

A better method is that proposed by Fordos and Gélis (*J. Pharm.* [3] xxiii. 48), depending on the reaction of iodine on cyanide of potassium. 5 grammes of the salt under examination are dissolved in water, and the solution is made up with water to half a litre. Of this solution 20 c. c. are introduced into a flask of about 2 litres capacity, together with a litre or  $1\frac{1}{2}$  litre of water. On the other hand, an alcoholic solution of iodine is prepared containing 40 grammes in a litre, and this standard liquid is poured from a burette (divided into cubic centimetres) into the solution of the cyanide, till the liquid becomes permanently yellow. The quantity of iodine required to produce this effect is then read off. 254 pts. iodine correspond to 65 pts. cyanide of potassium.

**CYANIDE OF PROPYL or TRITYL.**  $C^4H^7N = C^4H^7.CN$ .—Identical with BUTYRONITRILE (i. 698).



**CYANIDES OF RHODIUM.** The *sesquicyanide*,  $\text{Rh}^3\text{Cy}^2$ , is precipitated as a fine carmine-coloured powder, on adding strong acetic acid to a solution of potassio-rhodic cyanide. It dissolves in cyanide of potassium, and is decomposed by ignition, leaving metallic rhodium difficult to attack with acids. (Martius.)

*Potassio-rhodic Cyanide*,  $\text{K}^3\text{Rh}^2\text{Cy}^4 = 3\text{KCy}.\text{Rh}^2\text{Cy}^3$ , may be prepared like the corresponding iridium-salt (Claus, p. 323), or by igniting rhodium with ferrocyanide of potassium (Martius). It resembles the iridium-salt, but is distinguished therefrom by its reaction with acetic acid as just mentioned, the iridium-salt when treated in the same manner remaining unaltered. (Claus, Martius.)

**CYANIDES OF RUTHENIUM.** *Rutheniocyanide of Potassium*,  $\text{K}^3\text{Ru}^2\text{Cy}^4 + 3\text{aq.}$ , is obtained, like the iridium-salt, by fusing 1 pt. of chlororutheniate of ammonium with  $1\frac{1}{2}$  pts. pulverised cyanide of potassium, dissolving the fused mass in boiling water, and leaving the filtrate to cool. It crystallises in small transparent, colourless square tables, having their edges truncated by octahedral faces. It is isomorphous with ferrocyanide of potassium, and crystallises with that salt in all proportions; consequently it cannot be obtained pure by fusing ruthenium or any of its salts with ferrocyanide of potassium. When heated with hydrochloric acid, it gives off prussic acid, and after some time yields a deep violet-blue precipitate, consisting of cyanide of ruthenium mixed with a small quantity of cyanide of potassium. The solution of the salt treated with chlorine gas assumes a brown-yellow colour, quickly changing to dark green; probably a ruthenicyanide of potassium, analogous to the ferricyanide, is formed, but no crystalline compound is obtained.

The reactions of ruthenicyanide of potassium with metallic salts are similar to those of the ferro- and osmiocyanides (pp. 247, 259), viz. a light violet precipitate with *ferrous*, dark violet-blue with *ferric* salts; dirty red-brown with cupric salts; white with *mercurous* nitrate, acetate of *lead*, and sulphate of *zinc*; with *dichloride of platinum* it forms a dark brown solution. (Claus, Jahresb. d. Chem. 1856, p. 446.)

*Rutheniocyanide of Hydrogen*,  $\text{H}^4\text{Ru}^2\text{Cy}^4$ , is precipitated by hydrochloric acid and ether from the solution of the potassium-salt, in white nacreous laminae, which have a strongly acid, somewhat astringent taste, dissolve readily in water and in alcohol, and merely acquire a faint bluish colour when exposed to the air. (Claus.)

Ruthenium and osmium are the only metals of the platinum group whose potassio-cyanides are converted into hydrogen-salts in the manner just mentioned. (Claus.)

**CYANIDE OF SILVER.** *AgCy.*—Obtained by precipitating nitrate of silver with a soluble cyanide. According to Glassford and Napier, the purest product is obtained by using as the precipitant a solution of cyanide of silver and potassium.

Cyanide of silver is a white powder, insoluble in water, very slightly soluble in boiling dilute nitric acid, easily in ammonia. It is easily decomposed by hydrochloric and sulphydric acids. Heated in the dry state, it gives off half its cyanogen, with violent effervescence and a glow extending through the whole mass, and leaves a mixture of metallic silver and paracyanide of silver. (See PARACYANOGEN; also Gm. viii. 27.)

Cyanide of silver dissolves in the aqueous solutions of the cyanides of potassium, sodium, barium, strontium, and calcium, forming double cyanides,  $\text{MAgCy}^2$ , whose solutions are not precipitated, either by metallic chlorides or by caustic alkalis, but are decomposed by acids, with separation of cyanide of silver. It dissolves also at the boiling heat, in the chlorides of potassium, sodium, barium, calcium, and magnesium, and in ferro- or ferricyanide of potassium, the solution containing crystallisable cyanide of silver and potassium.

*Ammoniocyanide of Silver*, or *Cyanide of Argentammonium*,  $\text{NH}^4\text{AgCy}$ , is formed on pouring a dilute solution of nitrate of silver into a hot mixture of ammonia and prussic acid, and separates on cooling in large colourless plates, which give off all their ammonia when exposed to the air. (Liebig and Redtenbacher, Ann. Ch. Pharm. xxxviii. 129.)

*Nitrocyanide of Silver*,  $\text{AgNO}^3.2\text{AgCy}$ , is a crystalline salt obtained by dissolving recently precipitated cyanide of silver in a moderately concentrated and boiling solution of nitrate of silver.

*Cyanide of Silver and Potassium*,  $\text{AgKCy}^2 = \text{KCy}.\text{AgCy}$ , crystallises in colourless octahedrons, hexagonal plates, and rhomboïdal prisms, the latter when dried at  $100^\circ\text{C.}$  containing  $\frac{1}{2}$  at. water ( $\text{Ag}^2\text{K}^2\text{Cy}^4 + \text{aq.}$ ) (Glassford and Napier). It is permanent in the air, soluble in 8 pts. cold and 1 pt. boiling water; dissolves also in boiling alcohol, and crystallises therefrom on cooling (Glassford and Napier). According to S. Baup (Ann. Ch. Phys. [3] liii. 462), the pure salt crystallises on cooling in plumose lamellae, and by slow evaporation in six-sided prisms (the rhomboïdal prisms observed by Glassford and Napier consist of a cyanide of silver, potassium, and sodium to be presently noticed). It requires for solution 4 pts.

water at 20° C., and 25 pts. alcohol of 25 per cent. at the same temperature. It does not become coloured by exposure to sunlight, neither does it stain paper and the skin like other silver-salts. The cyanide of silver precipitated from the solution by nitric acid is likewise unalterable by light.

Cyanide of silver and potassium is used for galvanic gilding. When its solution is subjected to the action of the battery, metallic silver is deposited at the negative pole in a compact adhering layer, while at the positive pole, where a strip of silver is placed, a quantity of the metal is continually dissolving equal to that which is deposited at the other pole. The silver-bath may be prepared by dissolving cyanide, chloride, or any other silver-salt in cyanide, ferrocyanide, or ferricyanide of potassium.

*Cyanide of Silver and Sodium*,  $\text{NaAgCy}^2$ , obtained by saturating a solution of cyanide of sodium with cyanide of silver, forms anhydrous laminar crystals, soluble at 20° C. in 5 pts. of water and 24 pts. alcohol of 85 per cent. (Baup.)

*Cyanide of Silver, Potassium, and Sodium*,  $2\text{KAgCy}^2.\text{NaAgCy}^2$ , crystallises from the mother-liquor of commercial cyanide of silver and potassium, the sodium being derived from the impure potash used in the preparation of the cyanide of potassium. It crystallises in anhydrous rhomboïdal prisms, being in fact the salt regarded by Glassford and Napier as one of the forms of cyanide of silver and potassium. It dissolves in 4.4 pts. water at 15° C., and in 22 pts. alcohol at 17° C.

The solution of either of the double salts above mentioned forms white precipitates with the salts of *manganese, zinc, cadmium, lead, and mercuric*, greenish with *ferrous* salts, pale red with *cobalt*-salts, bluish-white with *cupric* salts, white with *mercuric* salts, all these precipitates consisting of compounds of cyanide of silver with another metallic cyanide.

**CYANIDE OF SODIUM**,  $\text{NaCy}$ , may be obtained by the same methods as cyanide of potassium, but does not form so easily. F. and E. Rodgers calcine 6 to 10 pts. prussian blue with 10 pts. dry carbonate of sodium, and exhaust the ignited mass with boiling alcohol, from which the cyanide of sodium crystallises.

**CYANIDE OF STYRYL**. *Cyanide of Cinnyl*.  $\text{C}^6\text{H}^5\text{N} = \text{C}^6\text{H}^5\text{Cy}$ .—Obtained by heating iodide of styryl with an alcoholic solution of cyanide of potassium in sealed tubes. On mixing the oily layer of liquid thereby produced with water, and adding chloride of sodium, the cyanide of styryl separates as a yellowish-oil, easily soluble in ether, slightly in alcohol, insoluble in water. When treated with potash, it gives off ammonia and becomes resinised. (Ramdohr, Zeitschr. Ch. Pharm. 1858, p. 113.)

**CYANIDE OF TETRYL**. *Cyanide of Butyl Valeronitrile*.  $\text{C}^4\text{H}^9\text{N} = \text{C}^4\text{H}^9\text{Cy}$ .—This body is produced by dehydrating valerate of ammonium,  $\text{C}^4\text{H}^9(\text{NH}^4)\text{O}^2$ , or valeramide,  $\text{N.H}^2.\text{C}^4\text{H}^9\text{O}$ , with anhydrous phosphoric acid (Dumas, Malaguti, and Leblanc, Compt. rend xxv. 658). It was discovered, in 1846, by Schlieper (Ann. Ch. Pharm. lix. 15) among the products of the decomposition of gelatin by chromic acid, and has been found by Guckelberger (*ibid.* lxiv. 72) among the products of the oxidation of casein.

*Preparation from Glue*.—2 pts. of glue are left to swell up in 50 pts. of water; 15 pts. of sulphuric acid are added; the mixture, after cooling, is poured into a retort containing 8 pts. acid chromate of potassium, and distilled till, towards the end, the liquid, which becomes continually greener, no longer boils quietly but begins to froth strongly. The distillate thus obtained—which is white and turbid, has an acid reaction, and smells strongly of hydrocyanic acid—is rectified over mercuric oxide, which decomposes the formic acid present, with evolution of gas, and retains the hydrocyanic acid in the form of cyanide of mercury; and the liquid which first passes over, mixed with oily drops, is collected apart and several times fractionally rectified *per se*, till the oil which passes over is accompanied by only a small quantity of watery liquid—then at a gentle heat over magnesia, to retain benzoic acid, the receiver being changed as soon as, in place of a transparent colourless oil and a clear watery liquid, a milky liquid, gradually depositing oily drops, begins to pass over. The first oil is dehydrated by means of chloride of calcium, and slowly distilled; the receiver changed at 110° C., because that which passes over at 90° is chiefly valeracetonitrile, while at 110° the mixture of that body with cyanide of tetryl, and from 110° to 140° principally the latter distils over; and this last distillate is subjected to two more distillations, the portion which distils over between 122° and 130° being collected apart in the former, and that which passes over between 124° and 127° in the latter: this latter portion is pure cyanide of tetryl. (Schlieper.)

*From Casein*.—1 pt. of casein is dissolved in a mixture of 3 pts. sulphuric acid and 6 pts. water contained in a retort; a solution of 2 pts. acid chromate of potassium in 10 pts. water is added (a larger quantity would produce valerianic acid instead of cyanide of tetryl); the reaction which ensues is moderated by the addition of 14 pts. more water (30 pts. in all); the distillate is shaken up and redistilled with mercuric oxide; the

distillate thus obtained is neutralised with chalk, and redistilled; and the neutral distillate is subjected to repeated fractional rectification, whereby there is obtained, first a milky distillate mixed with drops of colourless oil, and ultimately the latter only. When this distillate is further rectified, propylic aldehyde passes over below  $120^{\circ}$  C., and between  $120^{\circ}$  and  $140^{\circ}$  chiefly cyanide of tetryl, which may be purified by repeated rectification, the first and last portions that pass over being set aside. (Guckelberger.)

Cyanide of tetryl is a transparent, colourless, very thin liquid which refracts light strongly. Specific gravity  $0.81$  (Schlieper);  $0.813$  at  $16^{\circ}$  C. (Guckelberger). It boils at  $125^{\circ}$  (Schlieper); at  $125^{\circ}$  to  $128^{\circ}$  (Guckelberger). Vapour-density =  $2.892$  (Guckelberger). Smells like bitter almond oil and salicylic acid (Schlieper), and has an aromatic, burning, and bitter taste (Guckelberger). It makes a transient grease-spot upon paper. It dissolves in about four times its volume of water and mixes in all proportions with alcohol and ether. (Guckelberger.)

Cyanide of tetryl when set on fire, burns with a white luminous flame, and without smoke. In sunshine it is decomposed by chlorine or bromine, with formation of hydrochloric or hydrobromic acid (Schlieper). With strong sulphuric acid (also, according to Guckelberger, when distilled with dilute sulphuric acid), it is resolved into sulphate of ammonia and free valerianic acid (Schlieper):



Nitric acid, hydrochloric acid, and ammonia have no action upon it (Schlieper). With aqueous fixed alkalis, it is easily resolved into a valerate of the alkali-metal and free ammonia (Schlieper, Guckelberger). It is decomposed at ordinary temperatures by potassium, into cyanide of potassium, hydrogen gas, and a peculiar hydrocarbon. (Dumas, Malaguti, and Leblanc.)

**CYANIDE OF THALLIUM.** Precipitated, on cautiously adding cyanide of potassium to a solution of a thallium-salt, as a white or light brown powder, easily soluble in excess of the precipitant. (Crookes, Proc. Roy. Soc. xii. 156.)

**CYANIDE OF TITANIUM?** When the solution of crude platinum ore in aqua-regia is precipitated by cyanide of silver, cyanide of titanium is thrown down, together with the cyanide of palladium and copper. On igniting this precipitate in a retort, cyanide [or impure chloride?] of titanium sublimes in the form of a greyish-white mass, which dissolves readily in water, and is then precipitated white by ammonia, yellowish-red by tincture of galls, and gives a white colour with tin and hydrochloric acid. (Fr. Weiss and Fr. Döbereiner, Ann. Ch. Pharm. xiv. 16.)

*Nitrocyanide of Titanium*,  $\text{TiCy}^{\text{C}}.3\text{Ti}^{\text{C}}\text{N}^{\text{C}}$ .—This compound, which was formerly regarded as metallic titanium, occurs as a furnace-product, in the form of beautiful, opaque, copper-coloured crystals in the blast-furnaces in which iron is smelted. Its production appears to be connected with the formation of cyanide of potassium so constantly observed in the iron furnaces; a similar product is in fact obtained by placing a mixture of ferrocyanide of potassium and titanic acid in a well-closed crucible, and exposing it for an hour to a heat sufficient to melt nickel. The result is a brown unfused mass, which, under a magnifying power of 300 diameters, exhibits, besides particles of metallic iron, a network of short copper-coloured prisms having a strong metallic lustre. These crystals, when freed from iron by hydrochloric acid, exhibit all the properties of the crystals found in the blast-furnaces.

When this compound is heated to redness in a porcelain tube, and a continuous current of aqueous vapour passed over it, titanic acid is formed, with evolution of hydrogen gas in considerable quantity (Regnault), and likewise of ammonia and hydrocyanic acid (Wöhler). If the crystals are in their natural state (not pulverised), the titanic acid thus produced maintains the form of rounded cubes; but these, when examined by the microscope, are found to consist of aggregates of crystals, in the form of pointed square-based octahedrons, having a strong lustre and exactly resembling the crystals of native anatase.

The crystals of nitrocyanide of titanium heated in dry chlorine gas, yield liquid chloride of titanium, and a crystalline volatile yellow sublimate, consisting of a compound of chloride of titanium with chloride of cyanogen. Mixed in the state of powder with hydrate of potassium and fused, they give off ammonia and are converted into titanate of potassium. When the pulverised compound is heated with oxide of lead, copper, or mercury, a lively sparkling flame is emitted, and the oxide is reduced to the metallic state. The heat evolved in this reaction is so great that even copper runs into a globule in the glass tube. (Wöhler, Ann. Ch. Phys. [3] xxix. 166; Chem. Soc. Qu. J. ii. 252.)

**CYANIDE OF TIN.** Alkaline cyanides added to stannous salts throw down stannous hydrate, but retain a small portion of tin in solution. Stannous sulphide



dissolves slightly in boiling cyanide of potassium, and the solution is precipitated by hydrochloric acid.

**CYANIDE OF TRITYL.**  $C^3H^3N = C^3H^3Cy$ . (See BUTYRONITRILE, i. 698).

A compound of this body with trichloride of phosphorus,  $C^3H^3N.PCl_3$ , is obtained by treating butyramide with pentachloride of phosphorus. It is a colourless, strongly refracting liquid, which is decomposed by water, yielding cyanide of trityl, hydrochloric acid, and phosphorous acid. (Henke, Ann. Ch. Pharm. cvi. 272.)

**CYANIDES OF URANIUM.** Cyanide of potassium forms with uranic salts a yellow precipitate, soluble in nitric acid and in excess of cyanide of potassium. From uranous salts it merely precipitates uranous oxide.

**CYANIDE OF VANADIUM.** When hydrated vanadic oxide is digested in a close vessel with prussic acid, a dark brown gelatinous mass is produced which dissolves in aqueous cyanide of potassium; but the solution, when evaporated in an open vessel, gives off prussic acid and leaves vanadate of potassium. (Berzelius.)

**CYANIDE OF YTTRIUM.** The solution of hydrate of yttria in prussic acid yields on evaporation white efflorescent nodules easily soluble in water and alcohol. (Berlin.)

**CYANIDE OF ZINC,  $ZnCy$ .**—Zinc-salts mixed with an alkaline cyanide yield a white pulverulent precipitate of cyanide of zinc, insoluble in water and alcohol, but easily soluble in alkaline cyanides. Cyanide of zinc is likewise obtained by dissolving the oxide in hydrocyanic acid. C. Oppermann (J. Pharm. [3] xxxviii. 320) prepares it for medical purposes, by passing vapour of hydrocyanic acid into a solution of sulphate of zinc, mixed with 1 at. acetate of sodium, and slightly acidulated with acetic acid. The precipitate when washed is free from iron, even if it has been thrown down from an impure zinc-solution.

*Cyanide of Zinc and Ammonium*,  $(NH^4)ZnCy^2$ , forms colourless rhomboidal prisms which effloresce in contact with the air, and smell of hydrocyanic acid and ammonia. It is only partially soluble in water, cyanide of zinc remaining undissolved.

*Cyanide of Zinc and Barium*,  $BaZn^2Cy^3$ . White powder, sparingly soluble in water; precipitated on mixing the solutions of acetate of barium and cyanide of zinc and potassium. It generally retains a small quantity of potash.

*Cyanide of Zinc and Calcium.* Moderately soluble; obtained by treating cyanide of zinc with cyanide of calcium.

*Cyanide of Zinc and Lead.* White precipitate.

*Cyanide of Zinc and Potassium*,  $KZnCy^2$ , is obtained by dissolving cyanide of zinc in cyanide of potassium; crystallises in large regular octahedrons, colourless, fusible, having a saccharine taste and alkaline reaction, permanent in the air, very soluble in water. The aqueous solution has a faint odour of prussic acid. Small quantities of hydrochloric, sulphuric, or acetic acid precipitate the cyanide of zinc, but larger quantities of acid redissolve it. (L. Gmelin, Handb. vii. 424.)

*Cyanide of Zinc and Sodium*,  $NaZn^2Cy^3 + \frac{1}{2}aq$ .—Shining scales, which give off their water at  $200^\circ C$ .

**CYANIN.** *Anthokyan*. (Clamor Marquart, Die Farben der Blüten. Bonn, 1835.—Frémy and Cloëz, J. Pharm. [3] xxv. 249.—Filhol, Compt. rend. xxxix. 194.—Martens, Jahresb. d. Chem. 1855, 687.)—This name is applied to the blue colouring matter of flowers, which is perhaps identical with that of certain berries, roots, tubers, &c. It is contained in the blue petals of corn-flowers, violets, and several species of iris (*I. pumila* and *I. germanica*), and, according to Marquart, also in red, blue, and black flowers. To extract it, the petals are exhausted with alcohol; the liquid is evaporated to dryness; the residue treated with water, which separates a fatty or resinous substance, and dissolves the colouring matter; the aqueous solution is precipitated with acetate of lead; the green precipitate is washed, suspended in a large quantity of water, and decomposed by sulphydric acid; the filtrate is carefully evaporated over the water-bath; the residue treated with absolute alcohol; and the alcoholic solution mixed with ether, which precipitates the cyanin in blue flocks. (Frémy and Cloëz.)

Cyanin thus prepared is a blue uncrystallisable mass, soluble in water and alcohol, insoluble in ether. It is decolorised by reducing agents, such as sulphurous acid, phosphorous acid, and alcohol, but recovers its blue colour when exposed to the air. It is instantly coloured red by acids, green by alkalis. With bases, such as lime, baryta, and oxide of lead, it forms green insoluble compounds.

Red flowers are said also to owe their colour to the presence of cyanin reddened by a free acid. This supposition may account for the fact that many flowers, of the borage and mallow tribes, for example, which are red in the bud, turn blue when expanded,

and green as they fade, the change being due to the disappearance of the free acid, or to the formation of ammonia resulting from the decomposition of a nitrogenous compound.

The reaction of cyanin with acids and alkalis renders it useful for the preparation of test-paper and tinctures; the alcoholic extract of the petals of *Iris germanica* or *I. pumila* is very well adapted for the purpose.

The term cyanin is also applied to a blue dye, which, according to G. Williams (Dingl. polyt. J. clix. 330 and 399), is prepared from chinoline with iodide of amyl, and used in calico-printing. The colour is fugitive.

**CYANITE.** See KYANITE.

**CYANOCHROME.** A sulphate of copper and potassium,  $\text{CuKSO}_4 + 3\text{aq.}$ , found, together with other salts, as a deposit on the lava of Vesuvius thrown out in the eruption of 1855. (Scacchi, Sill. Am. J. [2] xxii. 252.)

**CYANOFORM?** A mixture of cyanide of mercury and dehydrated acetate of calcium yields by dry distillation a yellow liquid smelling of prussic acid, and, according to Bonnet (Gm. vii. 147), containing cyanoforn,  $\text{CHCy}^3$ , an analogue of chloroform. Bonnet, however, did not analyse the compound, and Nachbaur (Ann. Ch. Pharm. cx. 303), has shown that the liquid in question contains, together with cyanide of methyl, acetone, and prussic acid, a base having the composition of dicyanhexmethylidiamine,  $\text{C}^6\text{H}^{16}\text{N}^4 = \text{N}^2(\text{CH}^3)_4\text{Cy}^2$ . (See METHYLAMINES.)

**CYANOGEN.**  $\text{CN}$  (or  $\text{C}^2\text{N}$ ) = Cy.—This body, which exists, or may be supposed to exist, in a great number of compounds, the cyanides, cyanates, cyanurates, &c., was first obtained in the free state by Gay-Lussac in 1815, and afforded the first instance of the isolation of a compound radicle. Many of its compounds had been known long before, prussian blue having been discovered by Diesbach and Dippel in 1704, ferrocyanide of potassium by Macquer about the middle of the eighteenth century, and prussic acid by Scheele in 1782. The name cyanogen is derived from *κυανος* (blue) and *γεν*.

The modes of formation of cyanogen-compounds have already been mentioned (p. 198). Cyanogen is obtained in the free state by the action of heat on the cyanides of mercury, silver, and gold, or by the dry distillation of oxamide,  $\text{C}^2\text{H}^4\text{N}^2\text{O}^2$ , or oxalate of ammonium,  $\text{C}^2(\text{NH}^4)^2\text{O}^4$ , differing, in fact, from the former of these bodies only by  $2\text{H}^2\text{O}$ , and from the latter by  $4\text{H}^2\text{O}$ :



**Preparation.**—Dry cyanide of mercury is heated to low redness in a glass tube or small retort, and the cyanogen, which is evolved as gas, is collected over mercury. The mercury separated from the cyanogen volatilises and condenses in the colder part of the apparatus. A small portion of the cyanogen is converted into the isomeric compound *paracyanogen* (q. v.), and remains in the form of a brown loosely coherent mass. If the cyanide of mercury is moist, a large portion of the cyanogen is decomposed, with formation of ammonia, carbonic acid, and hydrocyanic acid.

The gas may likewise be obtained by heating in a retort an intimate mixture of 2 pts. (1 at.) of perfectly dried ferrocyanide of potassium,  $\text{K}^4\text{Fe}^2\text{Cy}^6$ , and 3 pts. (2 at.) of mercuric chloride:



Cyanogen is then evolved, mixed with vapour of mercury, and there remains a dark-coloured mixture of chloride of potassium and cyanide of iron. (Kemp, Phil. Mag. [3] xxii.)

**Properties.**—Cyanogen is a colourless gas, having a pungent odour very much like that of prussic acid. Its density, as determined by experiment, is 1.8064. Hence, as the molecular weight represented by the formula  $\text{CN}$  is  $26 \times 0.0693 = 1.802$ , it follows that, if the molecule of cyanogen occupies 2 volumes, like that of compound gases in general, it must be represented by the formula  $\text{C}^2\text{N}^2 = \text{Cy}^2$ .

Cyanogen condenses to a liquid under a pressure of about four atmospheres at mean temperatures (H. Davy and Faraday, Phil. Trans. 1823, p. 196), or by exposure to a temperature of  $-35^\circ$  or  $-40^\circ \text{C.}$  under the ordinary atmospheric pressure (Bunsen, Pogg. Ann. xlii. 101). A convenient mode of preparing liquid cyanogen is to heat cyanide of mercury in the longer arm of a strong tube, bent and sealed; the cyanogen then condenses in the shorter arm, which should be kept cold.

Liquid cyanogen is transparent, colourless, and very mobile (H. Davy and Faraday). Specific gravity at  $17.2^\circ = 0.866$  (Faraday). Refracting power = 1.316 (Brewster). It does not conduct the electricity generated by a battery of 300 pairs. (Kemp.)

Liquid cyanogen freezes at a few degrees below  $-30^\circ \text{C.}$ , forming a radiated icy



mass (Bunsen). Frozen cyanogen is transparent, crystalline, apparently of the same density as the liquid, and melts at  $-34.4^{\circ}$ . (Faraday, N. Bibl. Univ. lix. 162):

*Tension of Cyanogen expressed in Atmospheres.*

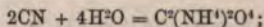
According to Faraday.						According to Bunsen.			
At.	Atm.	At.	Atm.	At.	Atm.	At.	Atm.	At.	Atm.
-12.2° C.	1.53	+6.9° C.	3.00	+21.1° C.	4.50	-20.7° C.	1.00	0° C.	2.7
6.7	1.89	8.9	3.17	23.3	4.79	20	1.05	+5	3.2
2.8	2.20	10.0	3.28	34.2	6.50	15	1.45	10	3.8
0	2.37	11.1	3.36	35.0	6.64	10	1.85	15	4.4
3.6	2.72	17.2	4.00	39.4	7.50	5	2.30	20	5.0

According to Niemann, the tension at 12.5 is equal to 4 atmospheres.

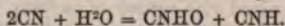
A mixture of equal parts of solid and liquid cyanogen (therefore at  $-34.4^{\circ}$  C.) does not exert a tension equal to the atmospheric pressure. When cyanogen evaporates into the air, an effect which takes place quietly on opening the containing vessel, the remaining portion does not freeze. (Faraday.)

*Decompositions.*—1. Cyanogen gas is not decomposed by passing through a red-hot tube.—2. When *electric sparks* are repeatedly passed through the gas, charcoal is deposited, and a volume of nitrogen set free equal to that of the gas. By the electric arc, this decomposition is effected in fifteen minutes at a temperature of  $30^{\circ}$  to  $40^{\circ}$  C. If the gas is moist, carbonic acid, carbonic oxide, and hydrogen are produced.—3. When set on fire in the *air*, it burns with a peach-blossom-coloured flame, producing carbonic anhydride and nitrogen.—4. Cyanogen mixed with excess of *oxygen* and set on fire by the electric spark, explodes violently, 1 vol. cyanogen consuming 2 vol. oxygen, and forming 2 vol. carbonic anhydride and 1 vol. nitrogen, so that the volume of the gas remains unaltered. The combustion of a mixture of cyanogen and oxygen is likewise induced by hot spongy platinum (Wöhler).—5. *Chlorine* does not act on cyanogen, even in sunshine, if both gases are perfectly dry; but if moisture is present, an oily body is formed, often mixed with a solid substance having an aromatic odour, and sparingly soluble in alcohol and ether.—6. *Hypochlorous anhydride* slowly decomposes cyanogen, forming carbonic anhydride, chlorine, nitrogen, and gaseous chloride of cyanogen. Aqueous *hypochlorous acid* in contact with cyanogen gives off the same four gases, with effervescence, the liquid afterwards containing hydrochloric and cyanic acids, and being covered with an oily mixture of chloride of cyanogen and chloride of nitrogen (Balard).—7. Cyanogen in contact with *manganic sulphate*, is resolved into carbonic anhydride and nitrogen (Berzelius).—8. When cyanogen is passed over red-hot metallic *iron*, the metal takes up carbon and becomes brittle, a coating of carbon is deposited upon it, and nitrogen is set free.

The solution of cyanogen in *water*, *alcohol*, or *ether* assumes a brown colour after a while, and deposits a dark brown powder called azulmic acid (i. 480), which, according to Pelouze and Richardson (Ann. Ch. Pharm. xxvi. 63), has the composition  $C^2N^4H^4O^2$ , that is to say, cyanogen together with the elements of water. The aqueous solution then contains cyanide, carbonate, and oxalate of ammonium, together with urea (Wöhler, Pogg. Ann. xv. 627). One part of the cyanogen takes up the elements of water and forms oxalate of ammonium:



while another portion is in like manner converted into cyanic and hydrocyanic acids:



The cyanic acid is immediately resolved into carbonic acid and ammonia (p. 191), which latter unites with another portion of the cyanic acid, forming urea (p. 193). This transformation of cyanogen is prevented by the presence of acids. If the water contains *aldehyde*, even in small quantity only, the cyanogen is converted into oxamide ( $C^2N^2 + 2H^2O$ ) without formation of a brown deposit. (Liebig.)

Cyanogen is absorbed by *potash-solution*, also by red-hot *carbonate of potassium*, forming cyanide and cyanate of potassium, the latter being quickly resolved in the solution into ammonia and carbonate of potassium. Cyanogen is abundantly absorbed by *ammonia*, the solution soon turning brown and yielding the same products that are formed in the decomposition of cyanogen by water.

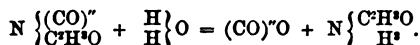
*Combinations.*—Cyanogen combines directly with *potassium* under the influence of heat. It also unites directly with *sulphydric acid gas*, in presence of water, and with certain organic bases, as *phenylamine*, *benzylamine*, *codeine*, &c. The bromide, chloride, and iodide of cyanogen, are formed by decomposing cyanides with *bromine*, *chlorine*, or *iodine*. The modes of formation of other cyanogen-compounds have already been given (p. 198).



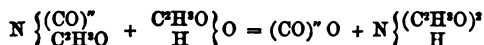
**CYANOGEN, ACETATE OF**, or *Cyanate of Acetyl*,  $\text{C}^2\text{H}^3\text{NO}^2 = \frac{\text{C}^2\text{H}^3\text{O}}{\text{CN}}\text{O}$ , or

*Carbacetamide*  $\text{N}\left\{\frac{(\text{CO})^{\text{r}}}{\text{C}^2\text{H}^3\text{O}}\right\}$  (Schützenberger, Ann. Ch. Pharm. cxxiii. 271).—When cyanate of silver is treated with chloride of acetyl in a cooled vessel, a dry pulverulent mass is formed containing acetate of cyanogen. On heating this mass to about  $100^{\circ}\text{C}$ ., carbonic anhydride is evolved, and a colourless very pungent liquid distillate passes over, boiling at  $80^{\circ}$  to  $85^{\circ}$ , and at higher temperatures an oily liquid, which solidifies to a mass of white needles.

The volatile liquid is a mixture of liquid acetate of cyanogen with cyanide of methyl, resulting from a decomposition of the former ( $\text{C}^2\text{H}^3\text{NO}^2 = \text{CO}^2 + \text{C}^2\text{H}^3\text{N}$ ). Water decomposes it, yielding carbonic anhydride and acetamide; a reaction which seems to indicate that the compound is really carbacetamide:



The white crystalline mass exhibits the composition of diacetamide, the formation of which is attributed by Schützenberger to the action of the acetate of cyanogen on acetic acid resulting from a secondary decomposition:



When acetate of silver is heated with iodide of cyanogen, iodide of silver is formed together with an explosive compound. (Schützenberger, Ann. Ch. Pharm. cxx. 118).

**CYANOGEN, BENZOATE OF**. When the product obtained by the action of chloride of benzoyl on cyanate of silver or cyanate of lead is heated, carbonic anhydride is evolved, and cyanide of phenyl passes over, produced apparently by the decomposition of benzoate of cyanogen;  $\text{C}^2\text{H}^3(\text{CN})\text{O}^2 = \text{CO}^2 + \text{C}^2\text{H}^3\text{N}$ . (Schützenberger.)

**CYANOGEN, BROMIDE OF**.  $\text{CNBr} = \text{CyBr}$ . Discovered and examined by Serullas in 1827 (Ann. Ch. Phys. [2] xxxiv. 100; xxxv. 294, 315), further examined by Löwig (*Das Brom und seine chemischen Verhältnisse*, Heidelberg, 1829, p. 69). It is produced by the action of bromine on cyanide of mercury, cyanide of potassium, or aqueous hydrocyanic acid.

*Preparation*.—1. When 1 pt. of bromine is poured upon 2 pts. of cyanide of mercury contained in a tubulated retort or glass tube closed at the bottom and surrounded with ice, bromide of mercury and bromide of cyanogen are formed, with great evolution of heat. The bromide of cyanogen sublimes in needles, contaminated at first with bromine, but ultimately the bromine flows back and enters completely into combination. Gentle heat is then applied, and the bromide of cyanogen sublimed into a receiver connected with the retort and surrounded with ice (Serullas).—2. Aqueous hydrocyanic acid is placed in a vessel surrounded with a frigorific mixture, and bromine added—in very small portions to prevent the temperature from rising too high—till the solution begins to assume a reddish tinge; the liquid, which is in process of solidification from the acicular crystallisation of the bromide of cyanogen, is then either expressed between blotting paper at a temperature below  $0^{\circ}\text{C}$ ., or it is gently heated to drive off the bromide of cyanogen in vapour, aqueous hydrobromic acid then remaining behind (Löwig).—3. Bromine and water are placed in a tube kept very cold, and cyanide of mercury and hydrochloric acid added till the red colour disappears; the open end of the tube is then drawn out to a narrow neck, which is sealed up, and the lower part of the tube is immersed in warm water, so that the bromide of cyanogen may sublime into the upper part (Mitscherlich, *Lehrbuch der Chemie*).—4. When bromine is added to an aqueous solution of cyanide of potassium cooled to  $0^{\circ}\text{C}$ ., crystals of bromide of cyanogen immediately separate. When the reaction is complete, these crystals may be separated from the solution of bromide of potassium by heating the liquid to  $60$ – $65^{\circ}\text{C}$ . (Langlois, Ann. Ch. Phys. [3] lxi. 482.)

*Properties*.—Bromide of cyanogen sublimes, at the first moment of its formation, in long delicate needles, which afterwards change to small transparent and colourless cubes (Serullas).—It melts at  $+4^{\circ}\text{C}$ . (Löwig), above  $+16^{\circ}$  (Serullas), not even at  $40^{\circ}$  (Bineau). Vapour-density = 3.607 (Bineau, Ann. Ch. Phys. [2] lxxviii. 425), by calculation (2 vols.) = 3.6745. Its boiling point is lower than that of iodide of cyanogen, and it volatilises even at  $16^{\circ}\text{C}$ . (Serullas). Its vapour has a very pungent odour; it excites a copious flow of tears, and is dangerous to inhale (Serullas); its taste is extremely biting (Löwig). One grain dissolved in water and poured into the œsophagus of a rabbit, kills it instantly (Serullas). It immediately

decolorises litmus and turmeric paper, and does not redden litmus even when dissolved in water (Löwig). It is very soluble in water and alcohol, and forms a crystalline hydrate which is less fusible than the anhydrous compound.

*Decompositions.*—1. Aqueous sulphurous acid forms with bromide of cyanogen: sulphuric, hydrobromic, and hydrocyanic acids.—2. Aqueous potash forms cyanide, bromide, and bromate of potassium (Serullas, Löwig). On adding to a saturated solution of bromide of cyanogen, first potash and then an acid, carbonic anhydride is evolved, and the liquid is afterwards found to contain ammonia (Serullas).—3. The aqueous solution mixed, first with ferrous sulphate, then with potash, and then with an acid, yields a green precipitate (Serullas); but if the potash be added first, then the ferrous sulphate, and then the acid, no precipitate is obtained (Serullas).—4. The aqueous solution of bromide of cyanogen, slowly evaporated to dryness, leaves hydrobromate of ammonia (Löwig). In this case carbonic anhydride should also be produced:  $\text{CNBr} + 2\text{H}^2\text{O} = \text{CO}^2 + \text{NH}^4\text{Br}$ .—5. Bromide of cyanogen gently heated with phosphorus, evaporates for the most part undecomposed; nevertheless, a small quantity of bromide of phosphorus is formed. Antimony, heated in vapour of bromide of cyanogen, yields cyanogen gas and bromide of antimony. Mercury decomposes the saturated aqueous solution, yielding cyanogen and bromide of mercury. (Löwig.)

Bromide of cyanogen dissolves without decomposition in strong sulphuric, hydrochloric, and nitric acids. It absorbs ammonia-gas, forming a mixture of bromide of ammonium and cyanamide (p. 188), which was regarded by Bineau as an ammonio-bromide of cyanogen.

**CYANOGEN, CHLORIDE OF.** Three chlorides of cyanogen are known, isomeric with each other, and having molecular weights in the proportion of 1 : 2 : 3. The first is gaseous at ordinary temperatures, the second liquid, and the third a crystalline solid.

*Gaseous Chloride of Cyanogen*,  $\text{CNCl} = \text{CyCl}$ .—This compound was first observed by Berthollet (Ann. Chim. i. 35), who, however, regarded it as oxidised prussic acid. Gay-Lussac (Ann. Chim. xc. 200) ascertained its true nature and examined it more fully; and it has been further investigated by Serullas (Ann. Ch. Phys. [2] xxxv. 291, 337; Pogg. Ann. xxi. 495), Wöhler (Ann. Ch. Pharm. lxxiii. 219), Cahours and Cloez (*ibid.* xc. 97), Cloez (*ibid.* cii. 354), Klein (*ibid.* lxxiv. 85), Martius (*ibid.* cix. 79), and Langlois (Ann. Ch. Phys. [3] lxi. 481).

Gaseous chloride of cyanogen is obtained by passing chlorine into aqueous prussic acid, or by leaving moist cyanide of mercury in contact with chlorine in a dark place. The former was the method by which Gay-Lussac obtained the gas, mixed, however, with carbonic acid; the latter method is now always adopted for preparing the gas in the pure state.

*Preparation.*—Cyanide of mercury moistened with water, but not dissolved in it, is introduced into bottles of a capacity not exceeding 3 litres, well closed with glass stoppers, and filled with chlorine gas, the proportion of cyanide of mercury being about 5 grammes to each litre of chlorine; the bottles are left for 24 hours in the dark, till in fact the chlorine has lost its yellow colour; then cooled by immersion in a mixture of ice and salt, producing a temperature at least as low as  $-18^\circ \text{C}$ , till the gaseous chloride of cyanogen solidifies in crystals. 100 grammes of water are then poured into each bottle; the resulting solution is poured from all the bottles into a long-necked flask, which it must nearly fill; and this flask is connected by a bent tube with a two-mouthed bottle containing chloride of calcium, so that the gaseous chloride of cyanogen may pass from its second mouth through a second bent tube into a bottle surrounded with a freezing mixture. If now the aqueous solution in the flask be warmed, the chloride of cyanogen collects in the crystalline form in the last bottle, which must then be closed very tight with a glass stopper. At ordinary temperatures, the crystals in the bottle melt, and are converted into gas. If, however, a small quantity of water be introduced into the bottle while it is immersed in the freezing mixture, and it be then taken out, still well closed, two layers are found in it, the upper of which is an aqueous solution of chloride of cyanogen, and the lower probably a hydrate of that compound. (Serullas). If the vessels are exposed to light, or if the temperature is allowed to rise to between  $30^\circ$  and  $40^\circ \text{C}$ , the chloride of cyanogen is decomposed.

Wöhler passes chlorine into a saturated solution of cyanide of mercury to which an excess of the salt in fine powder has been added, continuing the passage of the gas till the solution is completely saturated, and the upper part of the vessel filled with the gas. The vessel is then closed and left in the dark, till, after repeated agitation, the whole of the chlorine is absorbed, or the whole of the cyanide of mercury dissolved. To remove any remaining excess of chlorine, the solution is shaken up with mercury. It is then heated in a flask, which is connected with a chloride of calcium tube and a conducting tube, and the gaseous chloride of cyanogen is condensed as in the process last described.

Cahours and Cloez saturate 100 grm. cyanide of mercury and 4 litres of water, contained in a flask capable of holding 6 litres, with chlorine gas at  $0^{\circ}\text{C}$ . Hydrate of chlorine is then formed, which, in the course of 24 hours, is completely transformed, by the cyanide of mercury, into chloride of mercury and chloride of cyanogen, the latter remaining dissolved. The solution is slightly heated, and the gas thereby evolved, which generally contains a little free chlorine, is passed first over copper-turnings, and then over chloride of calcium.

According to Langlois, gaseous chloride of cyanogen is produced by the action of chlorine on a solution of cyanide of potassium cooled to  $0^{\circ}\text{C}$ ., and is given off as gas, partly at that temperature, partly when the action is ended, and the solution is heated to  $40^{\circ}$  or  $50^{\circ}\text{C}$ . If the solution of cyanide of potassium is not cooled, its temperature easily rises to  $80^{\circ}$  or  $90^{\circ}\text{C}$ ., and then other products are formed.

The extremely poisonous action of the gaseous chloride of cyanogen renders it necessary, in all these processes, to take the greatest care to prevent its escape into the air and consequent inhalation. For this reason, a freezing mixture made with chloride of calcium is preferable to the ordinary mixture of ice and salt.

*Properties.*—Chloride of cyanogen is, at ordinary temperatures, a colourless poisonous gas, having an intolerable odour, and exciting a copious flow of tears. Its specific gravity is 2.124 (by calculation for 2 vol., 2.128). At  $-12^{\circ}$  to  $-15^{\circ}\text{C}$ ., or at  $0^{\circ}\text{C}$ . under a pressure of four atmospheres, it condenses to a colourless liquid, which may be preserved in sealed tubes. At  $-18^{\circ}\text{C}$ . it crystallises in long transparent prisms. The gas, when kept in sealed tubes, is gradually converted into solid chloride of cyanogen,  $\text{Cy}^2\text{Cl}^2$ .

Water at  $20^{\circ}\text{C}$ . dissolves 25 times its volume of gaseous chloride of cyanogen, *either* 50 times, *alcohol* 100 times. When a small quantity of water is introduced into a bottle containing chloride of cyanogen and standing in a freezing mixture, two layers of liquid are formed, the upper consisting of an aqueous solution of chloride of cyanogen, the lower probably of a hydrate of that compound. The solutions of chloride of cyanogen, if free from hydrochloric acid, neither redden litmus nor precipitate solution of nitrate of silver. The aqueous solution appears to undergo gradual decomposition.

Potassium heated in gaseous chloride of cyanogen forms chloride and cyanide of potassium. Antimony heated in the gas forms chloride of antimony and liberates  $\frac{1}{2}$  vol. cyanogen. With *alkalis*, chloride of cyanogen forms a chloride and a cyanate:



When the aqueous solution of chloride of cyanogen is mixed, first with *ferrous sulphate*, then with potash, and then with an acid, a green precipitate is formed; but if the potash is added first, then the ferrous sulphate, and then the acid, no precipitation takes place. (Gay-Lussac, Serullas.)

Chloride of cyanogen mixed with *ammonia-gas* forms a mixture of sal-ammoniac and cyanamide (mistaken for Bineau for ammonio-chloride of cyanogen, p. 188). It acts in a similar manner on other volatile bases; with *ethylamine*, for example, it forms *cyanethylamide*. The *alcoholic* solution of chloride of cyanogen changes after some days into a mixture of hydrochloric acid or chloride of ammonium with carbonate and carbamate of ethyl. Similar products are obtained with *methyl*ic and *amylic alcohols* (Wurts). With a solution of *ethylate of sodium* in absolute alcohol, chloride of cyanogen forms chloride of sodium and cyanetholine (p. 189).

Chloride of cyanogen unites in definite proportions with certain other chlorides.

*Chloride of Cyanogen and Antimony*,  $\text{SbCl}^3.\text{CyCl}$ .—When gaseous chloride of cyanogen is passed over pentachloride of antimony, the latter becomes slightly heated, turbid, and gradually filled with delicate crystals. After saturation the compound forms a white crystalline mass. When heated, only a portion of it sublimates undecomposed, the greater part giving up its chloride of cyanogen. Water decomposes it instantly. It absorbs ammonia, with rise of temperature, forming a yellow pulverulent body. (L. Klein, Ann. Ch. Pharm. lxxiv. 87.)

*Chloride of Cyanogen and Boron*,  $\text{BCl}^3.\text{CyCl}$ .—Liquid chloride of boron absorbs dry chloride of cyanogen, with great evolution of heat, and forms a white loose crystalline mass. If the saturation is not quite complete, the compound separates gradually in small colourless prisms. It smells of chloride of cyanogen, fumes in damp air, and is decomposed by water, with rise of temperature, into boric acid, hydrochloric acid, and gaseous chloride of cyanogen. It acts in like manner on absolute alcohol. It sublimates with partial decomposition when strongly heated, leaving a white substance. (Martius.)

*Chloride of Cyanogen and Iron*,  $\text{Fe}^2\text{Cl}^3.\text{CyCl}$ .—Sublimed sesquichloride of iron absorbs gaseous chloride of cyanogen, with evolution of heat, fusing with it into a black mass; the compound was not, however, obtained in a complete state of saturation. When heated it fuses, swells up, and gives off gaseous chloride of cyanogen; it is re-



markable, however, that this decomposition likewise yields solid chloride of cyanogen sublimed in crystals. (Klein.)

*Chloride of Cyanogen and Titanium*,  $\text{TiCl}_4 \cdot \text{CyCl}$ .—Gaseous chloride of cyanogen acts instantly, and with great evolution of heat, on tetrachloride of titanium, converting it into a bulky, yellow, crystalline mass, which must be shaken up and heated gently, in order that it may be completely saturated with the chloride of cyanogen.

Lemon-yellow, very volatile; begins to volatilise considerably below  $100^\circ$ , subliming in clear lemon-yellow crystals which appear to be rhombic octahedrons. It fumes very strongly in damp air, quickly becoming milk-white, and exhaling the odour of chloride of cyanogen. Water dissolves it, with great rise of temperature and evolution of chloride of cyanogen, forming a clear solution. It dissolves without alteration in warm tetrachloride of titanium, separating out again in crystals on cooling. It absorbs ammonia, with great rise of temperature, forming with it an orange-red compound, which also turns white in moist air, and is decomposed by water, with partial separation of titanous anhydride. (Wöhler.)

*Chloride of Cyanogen with Cyanide of Ethyl*,  $\text{CyCl} \cdot \text{C}_2\text{H}_5\text{N}$ .—Dry gaseous chloride of cyanogen is rapidly absorbed by cyanide of ethyl, producing a colourless liquid which boils between  $60^\circ$  and  $68^\circ \text{C}$ ., and exerts an intensely irritating action on the eyes and the respiratory organs. It is decomposed, with rise of temperature, by water, and decomposes spontaneously when left for several days, the whole of the chloride of cyanogen being separated as solid chloride of cyanogen,  $\text{Cy}^2\text{Cl}^2$ . (Henke, Ann. Ch. Pharm. cvi. 289). [For the compound of chloride of cyanogen with cyanide of hydrogen, see below.]

2. *Liquid Chloride of Cyanogen*,  $\text{C}^2\text{N}^2\text{Cl}^2 = \text{Cy}^2\text{Cl}^2$ .—This compound, discovered by Wurtz (Ann. Ch. Pharm. lxiv. 308; lxxix. 280), is prepared by slowly passing chlorine gas into hydrocyanic acid, cooled to  $0^\circ \text{C}$ . in a retort connected with a cooled receiver, as long as the gas continues to be absorbed. The liquid in the retort then separates into two layers, the lighter consisting of hydrocyanate of chloride of cyanogen,  $\text{Cy}^2\text{Cl}^2 \cdot \text{HCy}$ , part of which is generally carried over into the receiver. From this compound the liquid chloride of cyanogen may be obtained, by mixing it, after separation from the heavier liquid, with ice-cold water, and treating it with mercuric oxide, which decomposes the hydrocyanic acid, care being taken to cool the vessel well, as otherwise the mercuric oxide may be reduced. Chloride of calcium is then added, the liquid distilled, and the vapour passed through a tube containing chloride of calcium into a flask cooled to  $0^\circ \text{C}$ . The chloride of cyanogen then condenses in the form of a very mobile colourless liquid, having an extremely pungent and exciting odour, and heavier than water, in which it is slightly soluble.

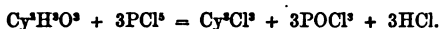
Liquid chloride of cyanogen solidifies in the crystalline form at  $5^\circ$  or  $6^\circ \text{C}$ ., and boils at  $15.5^\circ \text{C}$ . Its vapour is not inflammable. When pure, it may be kept for years in sealed tubes without passing into the state of solid chloride of cyanogen. If, on the contrary, chlorine in excess be passed into dilute prussic acid, and the liquid which separates be distilled without previous washing and treatment with mercuric oxide, an impure product is obtained which changes into solid chloride of cyanogen in the course of twenty-four hours. The same transformation takes place also in twenty-four hours, in chloride of cyanogen prepared by the action of chlorine on dry cyanide of mercury; after washing, however, it no longer exhibits this property. (Wurtz.)

Ammonia-gas converts liquid chloride of cyanogen into cyanamide and sal-ammoniac.

*Hydrocyanate of Chloride of Cyanogen*,  $\text{Cy}^2\text{Cl}^2 \cdot \text{HCy}$ .—Obtained by the action of chlorine on aqueous hydrocyanic acid in the manner above described. It is a colourless liquid, smelling strongly of chloride of cyanogen, inflammable, and burning in the air with a violet flame. It boils at about  $20^\circ \text{C}$ ., and solidifies perfectly in a mixture of ether and solid carbonic acid. In the pure state it may be kept for years without colouring or depositing crystals. It is perceptibly soluble in water; but a large quantity of water decomposes it, abstracting the hydrocyanic acid. In an atmosphere of chlorine it changes in about twenty-four hours into solid chloride of cyanogen. Bromine converts it into a semi-solid mass, which, when moderately warmed, gives off bromide of cyanogen, and at a higher temperature yields solid chloride of cyanogen. Mercuric oxide abstracts the hydrocyanic acid, and converts the compound into liquid chloride of cyanogen. (Wurtz, loc. cit.)

3. *Solid Chloride of Cyanogen*,  $\text{C}^2\text{N}^2\text{Cl}^2 = \text{Cy}^2\text{Cl}^2$ .—This compound was discovered in 1827 by Serullas (Ann. Ch. Phys. [2] xxxv. 291, 337), who regarded it as a bichloride of cyanogen; its true composition was demonstrated by Liebig (Pogg. Ann. xx. 369; xxxiv. 604). It is produced: 1. By the spontaneous transformation of gaseous chloride of cyanogen and of the impure liquid chloride.—2. By the action of excess of chlorine in sunshine on anhydrous prussic acid or on moist cyanide of mercury, by which reactions it was indeed first obtained by Serullas.—3. By heating dry sulpho-

cyanate of potassium in chlorine gas (Liebig).—4. By the action of pentachloride of phosphorus on dry cyanuric acid (Beilstein, Ann. Ch. Pharm. cxvi. 357):



*Preparation.*—1. Chlorine in excess is passed into dilute hydrocyanic acid, and the liquid which separates (p. 280) is distilled without previous purification. The liquid chloride of cyanogen which passes over soon changes into the solid modification (Wurtz). This is one of the easiest modes of preparation.

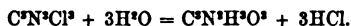
2. A bottle of 1 litre capacity is filled with dry chlorine gas; 0.82 grm. of prussic acid, prepared by Gay-Lussac's method, introduced into it; and the closed bottle exposed to the sun for one to three days, whereupon the hydrocyanic acid evaporates, the chlorine gas is decolorised, and a transparent colourless liquid formed, which runs down the sides of the vessel, and soon solidifies in white crystals of solid chloride of cyanogen. The hydrochloric acid gas, together with any volatile chloride of cyanogen that may be present, is then blown out of the bottle with a pair of bellows; a small quantity of water and a few pieces of glass are introduced, in order to detach the crystallised solid chloride of cyanogen from the sides of the vessel by agitation; the whole is poured into a basin; the pieces of glass are taken out; the solid chloride of cyanogen is comminuted with a glass rod, and repeatedly washed on a filter with a small quantity of cold water, till the liquid which runs away no longer forms a cloud with nitrate of silver\*; the solid chloride of cyanogen is pressed between bibulous paper, till it is converted into a dry white powder; and this powder is purified by one or two distillations from a small retort, whence it passes in the form of a transparent colourless liquid into a receiver cooled with wet linen, and there solidifies. (Serullas.)

3. When dry cyanogen gas is passed over heated sulphocyanate of potassium, solid chloride of cyanogen partly sublims in needles, partly distils over dissolved in chloride of sulphur. The needles are purified from adhering chloride of sulphur by a second sublimation in a vessel through which a continuous stream of chlorine gas is passed. The chloride of sulphur which passes over, leaves when evaporated an additional quantity of crystals of solid chloride of cyanogen, together with a yellow liquid having a high boiling point. From this residue, the chloride of cyanogen is separated by sublimation in a stream of chlorine gas, the yellow liquid then remaining behind. (Liebig.)

4. Perfectly dry cyanuric acid is well mixed with about six times its weight of pentachloride of phosphorus; the mixture is distilled; the distillate, consisting of oxychloride of phosphorus holding solid chloride of cyanogen in solution, is treated with water to decompose the oxychloride; and the solid chloride of cyanogen which then separates is washed with water and crystallised from ether. This method yields a perfectly pure product. To ensure success, however, the quantity of cyanuric acid operated upon must be somewhat considerable. The decomposition may also be effected in sealed tubes at 150°—200° C.; but this method is less convenient. (Beilstein.)

*Properties.*—Shining white needles of specific gravity about 1.320, melting at 140° C. to a transparent colourless liquid, and boiling at 190° (Serullas). Vapour-density 6.35 (Bineau, Ann. Ch. Phys. [2] lxxvii. 424), by calculation (2 vol.) = 6.385. It gives out, especially when heated, a pungent odour like that of chlorine, but at the same time strongly resembling that of mice, and excites tears. Its taste is weak, but is nevertheless similar to the odour. One grain dissolved in alcohol and introduced into the alimentary canal of a rabbit, kills it instantly. (Serullas.)

Solid chloride of cyanogen dissolves in water without decomposition at first, but is afterwards resolved with it, slowly at ordinary temperatures, more quickly at the boiling heat, and instantly in presence of a fixed alkali, into hydrochloric and cyanuric acids (Serullas):



Similarly, when boiled with ammonia, water, and alcohol, it yields sal-ammoniac and cyanuric acid; but in the absence of alcohol, chlorocyanamide is produced. The same compound is formed, with slight evolution of heat, when dry ammoniacal gas is passed over pulverised chloride of cyanogen (Liebig). Solid chloride of cyanogen mixed with potassium is decomposed, with evolution of light and heat, yielding chloride and cyanide of potassium (Serullas). It dissolves very readily in alcohol and ether, whence it is precipitated by water. When dissolved in absolute alcohol it remains unaltered; but in hydrated alcohol, it is converted in a short time, with violent evolution of heat, into vapour of hydrochloric acid, and cyanuric acid, which settles in cubes at the bottom of the liquid. (Liebig.)

\* This wash-water, which contains hydrochloric acid, cyanuric acid, and a small quantity of chlorocyanic oil, may be used for the preparation of cyanuric acid.



**Chlorocyanic Oil.**—This name is given to an oily liquid containing chlorine, carbon, and nitrogen, which is produced by the action of chlorine on many cyanogen-compounds, *e.g.* on cyanogen-gas in sunshine (Gay-Lussac, *Ann. Chim.* xcv. 200), on anhydrous hydrocyanic acid in sunshine (Gay-Lussac, Serullas, *Ann. Ch. Phys.* [2] xxxv. 300), on the strong aqueous acid (Gay-Lussac), on dry cyanide of mercury in sunshine. (Gay-Lussac.)

**Preparation.**—A concentrated aqueous solution of 5 grms. cyanide of mercury is poured into a bottle of 1 litre capacity, filled with chlorine gas and exposed to the sun: in an hour or two, drops of oil are seen running down the sides, and in four hours, if the sunshine is strong, the action is complete. In diffused daylight, the decomposition goes on more slowly and yields less oil. The oil is mechanically separated from the water above it—a large quantity of volatile chloride of cyanogen then escaping—and drawn up into tubes under water (Serullas). Bouis (*Ann. Ch. Phys.* [3] xx. 446) proceeds in the same manner, except that he prepares a solution of cyanide of mercury saturated at the boiling heat, and pours it while still hot into bottles filled with chlorine. The crystals of chloride of mercury which form at first, soon dissolve, and are replaced by elongated crystals, the formation of which appears, however, to be merely accidental; afterwards the oily drops appear. The chlorine must be repeatedly renewed, till it no longer loses its colour. In the bright sunshine of summer, the saturation of the liquid with chlorine is completed in two hours; in winter it takes two or three weeks. Four parts of cyanide of mercury yield 1 pt. of the oil.

Chlorocyanic oil is a yellow liquid, heavier than water; it has a very caustic taste (Bouis), and a very pungent odour, like that of cyanogen, but with a peculiar aromatic character, causing a copious flow of tears and coughing. It is not nearly so poisonous as chloride of cyanogen, a tolerably strong dose killing rabbits only after several hours. When recently prepared, it does not redden litmus or precipitate nitrate of silver (Serullas). Its boiling point is at least as high as that of oil of vitriol (Liebig). It makes grease-spots on paper, which are dissipated by heat. It is insoluble in water, but soluble in alcohol and ether. It decomposes gradually, whether moist or dry, depositing crystals of trichloride of carbon,  $C^3Cl^4$ . It explodes when heated. Bouis found it to contain 10.6 per cent. carbon, 8.4 nitrogen, and 75.6 chlorine, whence he deduces the formula  $C^4N^4Cl^{14}$ . Serullas regards it as a mixture of chloride of cyanogen with chloride of carbon and chloride of nitrogen.

The oil, when moderately heated, boils, gives off nitrogen (mixed with carbonic anhydride), and yields a liquid distillate which deposits crystals of trichloride of carbon. The distillate is colourless, limpid, heavier than water; has a strong irritating odour; is insoluble in water, soluble in alcohol, more soluble in ether; boils at about  $85^{\circ}C$ , the boiling point, however, gradually rising. Bouis found in it 11.6—12.4 per cent. carbon, 4.9 to 5.1 nitrogen, and 80.4—81.8 chlorine, and represents it by the formula  $C^6N^4Cl^{12}$ .

When the chlorocyanic oil is slightly heated with nitric acid, the mixture gives off torrents of gas, which often blow the apparatus to pieces. The gases consist of nitrogen, carbonic anhydride, and nitrous vapours, mixed with a yellowish vapour having a very powerful odour. By distillation, crystals of trichloride of carbon are obtained, together with a colourless, very volatile liquid, having an odour still more irritating than the preceding products. Bouis found it to contain 10.3 to 10.9 per cent. carbon, 8.2 to 7.85 nitrogen, and 75.9 to 75.7 chlorine, numbers which he represents by the formula  $C^{12}N^4Cl^{14}O^2$ .

In connection with these compounds, we may describe a crystalline substance, which Stenhouse (*Ann. Ch. Pharm.* xxxiii. 92) obtained by the action of dry chlorine on an alcoholic solution of cyanide of mercury, or of hydrocyanic acid.

When an alcoholic solution of cyanide of mercury, cooled by cold water, is saturated with dry chlorine gas, large quantities of sal-ammoniac are produced; the mass becomes heated, giving off carbonic anhydride with effervescence, and the liquid retains a peculiar compound, together with mercuric chloride. The solution is heated with water, which dissolves the sal-ammoniac and the chloride of mercury, and deposits the new body in white shining needles. If boiling water is used, the crystals form slowly and are of larger size. Care must be taken not to let the liquid get heated during the passage of the chlorine, and to stop the current of gas as soon as sal-ammoniac ceases to be deposited, otherwise secondary products will be formed. A more economical mode of preparation is to pass chlorine slowly into a strong alcoholic solution of hydrocyanic acid till crystals of sal-ammoniac make their appearance, and the liquid gives off carbonic anhydride with effervescence.

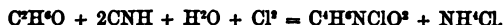
The compound crystallises in long, colourless, shining needles, much like sulphate of quinine. It is neutral, tasteless, inodorous, and melts at  $120^{\circ}C$ . with partial sublimation. It dissolves sparingly in cold water, easily in alcohol and ether. Potash-ley decomposes it, ammonia being given off, and the liquid assuming a dark brown



## CYANOGEN, DETECTION AND ESTIMATION OF. 283

colour. It dissolves in hot aqueous ammonia, and separates out on cooling. Sulphuric acid and nitric acid likewise dissolve it.

This substance gives by analysis (mean) 35.4 per cent. carbon, 5.0 hydrogen, 10.35 nitrogen, and 26.0 chlorine, whence Stenhouse deduces the formula  $C^4H^1ClN^3O^2$ . Laurent supposes it to contain 1 at. hydrogen less, and represents it by the formula  $C^4H^0N.ClO^2$ , supposing it to be formed as shown by the equation:



The evolution of carbonic anhydride is ascribed to a secondary reaction. According to Laurent's formula, the body might be resolved into oxalic acid, alcohol, and sal-ammoniac:



**CYANOGEN, DETECTION and ESTIMATION OF.** The detection of cyanogen in *metallic cyanides* which give off prussic acid when treated with dilute acids, is very simple, especially when only the alkali-metals or alkaline-earth-metals are present. The liquid is first rendered strongly alkaline (if not so already); a small quantity of a ferroso-ferric solution is added; and the mixture is warmed for a short time (to favour the formation of yellow prussiate), then supersaturated with hydrochloric acid. Prussian blue is then formed if a cyanide is present, or if in very small quantity, the liquid assumes a green colour, and slowly deposits prussian blue on standing, the green colour of the liquid changing at the same time to yellow. (See also *TESTS FOR HYDROCYANIC ACID*, p. 218.)

To detect cyanogen in *double cyanides* which do not give off prussic acid with dilute acids, they must first be fused with dry carbonate of sodium, the mass then lixiviated with water, and the solution tested with a ferroso-ferric salt as above.

The detection of cyanogen in its other compounds is more difficult. The *cyanates*, *sulphocyanates*, and *cyanamides* are not easily converted into cyanides; most of them, however, exhibit reactions of their own, by which they may be easily recognised, *e.g.* cyanic acid by splitting up with water into ammonia and carbonic acid; sulphocyanic acid by the blood-red colour which it produces with ferric salts. Chloride, bromide, and iodide of cyanogen, mixed first with solution of ferrous sulphate and then with potash-ley, yield a green precipitate after acidulation with hydrochloric acid.

From the *cyanides of the alcohol-radicles and organic bases*, such as cyanophenylamine, the cyanogen cannot be separated as such, so that it is doubtful whether these compounds actually contain cyanogen. On treating them with acids or alkalis, ammonia is separated, and the carbon of the cyanogen is left in combination with the remaining carbon of the organic body, *e.g.*



Cyanide of  
phenylamine.

Phenylox-  
amide.



Cyanide of  
ethyl.

Propionate of  
potassium.

To test a *gas* for cyanogen, the gas is shaken up with potash-ley, which absorbs the cyanogen, forming cyanide and cyanate of potassium; the solution may then be tested with a ferroso-ferric salt as above. The same reaction will however be obtained if the gas contains hydrocyanic acid instead of cyanogen; but in that case no cyanate of potassium will be formed. The potash-solution must therefore be further tested for cyanate by acidulating it with hydrochloric acid, and heating gently; the cyanic acid will then be resolved into carbonic acid and ammonia, which latter will be given off on supersaturating with potash. Another method of detecting free cyanogen in presence of hydrocyanic acid, is to remove the latter by means of red mercuric oxide, which does not absorb the cyanogen at all if dry, and only very slowly if it is moist. The remaining gas may then be tested with potash as above.

The *quantitative estimation* of cyanogen may often be effected by loss, that is to say, by determining the amount of the body (generally a metal) united with the cyanogen. To determine the cyanogen directly, the cyanogen-compound is generally burnt in a combustion-tube with oxide of copper, and the carbon determined as in organic analysis. 100 pts. by weight of carbonic anhydride,  $CO^2$ , are equivalent to 59.1 pts. cyanogen, CN.

If other compounds are present containing carbon, but free from nitrogen, the cyanogen may be converted into ammonia by ignition with soda-lime, and the

ammonia quantitatively determined. 100 pts. ammonia correspond to 152.94 pts. cyanogen.

In cyanides which are soluble in water or in dilute acids, the amount of cyanogen may generally be determined by precipitation with nitrate of silver as described in the article CYANIDE OF HYDROGEN (p. 219). In some cases, however, as with cyanide of mercury and many double cyanides, *e. g.* the ferro-ferric and cobaltcyanides, this method is not directly applicable; such compounds must be treated by some of the methods previously mentioned.

The amount of cyanogen in *cyanide of mercury* may be accurately determined by mixing the aqueous solution of the salt with caustic potash and sulphide of potassium, the latter in slight excess only, and adding a solution of zinc-oxide in potash. The cyanogen may then be precipitated from the neutralised filtrate by nitrate of silver. When cyanide of mercury is decomposed by sulphydric acid, part of the cyanogen is sure to escape as hydrocyanic acid. Another very exact method is to decompose the mercuric cyanide, dissolved in more than 25 to 30 pts. water in a stoppered bottle with cadmium filings. The decomposition is complete in about 36 hours, and the cyanogen may then be precipitated from the solution of cyanide of cadmium by nitrate of silver. (H. Rose, *Zeitsch. Anal. Chem.* i. 288.)

**CYANOGEN, IODIDE OF.** CNI = CyL (H. Davy, *Gilb. Ann.* liv. 384. Wöhler, *ibid.* lxi. 281. Serullas, *Ann. Ch. Phys.* [2] xxvii. 184; xxix. 184; xxxiv. 100; xxxv. 293, 344. Van Dyk, *Repert. Pharm.* xxi. 223.) This compound, discovered by Sir H. Davy in 1816, is not formed by the direct union of its elements, but is easily obtained by the action of iodine on cyanide of mercury, cyanide of silver, or other metallic cyanides; it is likewise found as an impurity in commercial iodine (Scanlan, *Chem. Soc. Mem.* iii. 321. F. Meyer, *Arch. Pharm.* [2] li. 29. Klobach, *ibid.* lx. 34).—1. Two pts. of cyanide of mercury are mixed with 1 pt. of iodine, very intimately, but quickly, to prevent loss by volatilisation, and the mixture gradually and gently heated, either in a retort provided with a receiver, or in a wide-necked flask, the mouth of which passes under a bell-jar partly closed with a glass plate; or the mixture is heated in a small porcelain dish till the iodide of cyanogen begins to volatilise, the dish then placed upon a large glass plate, and covered with a bell-jar; the iodide of cyanogen then sublimes on the sides of the jar in large white flocks (Serullas). The product is usually contaminated with iodide of mercury, which sublimes with the iodide of cyanogen, chiefly towards the end of the operation; it may be purified by a second sublimation over the water-bath or in sunshine, but the operation takes a long time. If the iodide of cyanogen, when supersaturated, first with strong aqueous potash and then with nitric acid, yields no precipitate of mercuric iodide, it may be considered free from that impurity. (Serullas.)

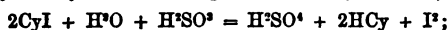
2. By heating a mixture of iodine and cyanide of silver. This process yields a purer product (Wöhler)—134 pts. (1 at.) cyanide of silver require rather less than 252 pts. (2 at.) of iodine.

3. Iodine is dissolved in a concentrated solution of cyanide of potassium, in such quantity that the solution may solidify in a crystalline mass on cooling, and the solid mass is gently heated till the iodide of cyanogen sublimes. (Liebig, *Chim. org.* i. 180.)

*Properties.*—Iodide of cyanogen forms long, white, very delicate needles, loosely united in feathers and stars (Serullas). From its solution in ether or absolute alcohol, it crystallises in small four-sided tables; from a solution in spirit of 80 per cent., in long feathery needles (Herzog, *Arch. Pharm.* [2] lxi. 129). It is very heavy, sinking rapidly in oil of vitriol. It boils at a temperature considerably above 100° C., and volatilises undecomposed even at ordinary temperatures. It has a highly penetrating and pungent odour of iodine and cyanogen together; excites a copious flow of tears; and has an extremely acrid taste (metallic if it is contaminated with iodide of mercury) (Serullas). It is very poisonous, acting like iodine and cyanogen together. It dissolves in *water*, and more readily in *alcohol*, forming colourless solutions which do not change the colour of litmus or turmeric, or turn starch blue, or precipitate nitrate of silver. It dissolves with still greater facility in *ether* and in *volatile oils*, and is likewise soluble in *fixed oils*.

*Decompositions.*—1. Iodide of cyanogen thrown upon red-hot coals (Serullas), or passed through a red-hot tube (Wöhler), gives off violet vapours of iodine. Even its aqueous solution, when kept for some time, imparts a pale violet colour to the superincumbent air (Serullas). Strong *sulphuric acid* decomposes iodide of cyanogen very slowly, acquiring thereby a red colour, and precipitating iodine (Serullas); according to Herzog, the decomposition does not take place without the aid of heat. It dissolves also without decomposition in *nitric* and in *cold hydrochloric acid*.—3. *Sulphurous anhydride* exerts no action on iodide of cyanogen; but the aqueous solution of sulphurous acid forms with it (water being decomposed) sulphuric acid,

hydrocyanic acid and iodine, which last substance, by the further action of the sulphurous acid, yields hydriodic and sulphuric acids. (Serullas):



and:



*Sulphydic acid gas*, in the absence of water, converts iodide of cyanogen into hydriodic acid and black iodide of sulphur; in presence of water, the products are hydrocyanic acid, hydriodic acid, and a precipitate of sulphur:



and:



5. Iodide of cyanogen dissolves in *caustic potash*, forming cyanide, iodide, and perhaps also iodate of potassium (Serullas). Probably thus:



6. An aqueous solution of iodide of cyanogen mixed, first with potash, then with *ferrous sulphate*, then with hydrochloric acid,—or first with ferrous sulphate, then with potash, and then with hydrochloric acid,—yields a green precipitate (Serullas). This reaction distinguishes iodide of cyanogen from the bromide and chloride, which yield the green precipitate in the latter case only.—7. *Phosphorus* melts in contact with iodide of cyanogen, and yields iodide of phosphorus, often with emission of light and heat; the cyanogen is probably set free in this reaction (Wöhler, Dyk). Similarly, powdered *antimony* heated with iodide of cyanogen decomposes it with noise, and forms iodide of antimony; and *mercury* agitated with aqueous iodide of cyanogen liberates the cyanogen, and is converted into iodide of mercury, exhibiting first a yellow and then a red colour. (Wöhler.)

Dry chlorine gas and nitric acid do not decompose iodide of cyanogen. (Serullas.)

With *ammonia-gas*, iodide of cyanogen forms a mixture of iodide of ammonium and cyanamide, formerly regarded as ammonio-iodide of cyanogen. (See CYANAMIDE, p. 188.)

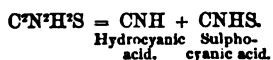
**CYANOGEN, SULPHYDRATES OF.** Dry sulphydic acid gas does not act upon cyanogen, but in the moist state, the two gases unite, forming two crystalline compounds, according to the proportions in which they are mixed.

*Monosulphhydrate. Flaveanwasserstoffsäure* (Berzelius). *Sulphoxalenide* (Laurent).  $\text{C}^2\text{N}^2\text{H}^2\text{S} = \text{Cy}^2.\text{H}^2\text{S}$ .—This compound is formed when cyanogen and sulphydic acid gas, both moist and the former in excess, are passed into a glass receiver standing over mercury, or into alcohol. Laurent (Compt. chim. 1860, p. 373) passes the two gases (the cyanogen in large excess) into a large bottle moistened with water, and purifies the crystals which form, by recrystallisation from ether.

The compound crystallises in yellow needles having a pungent and afterwards bitter taste. It dissolves in water, alcohol, and ether. The solutions are not acid; they become darker-coloured on standing, and deposit brown flocks, emitting at the same time an odour of prussic acid. Heated with dilute acids or alkalis, it yields oxalic acid, ammonia, and sulphydic acid:



With a strong solution of potash, it forms sulphocyanate and cyanide of potassium:

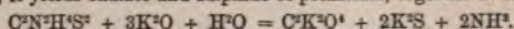


With silver-salts, it forms sulphide of silver, cyanogen being at the same time set free; from acetate of lead, after a while, it precipitates sulphide of lead.

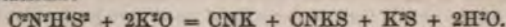
*Disulphhydrate. Rubranwasserstoffsäure* (Berzelius). *Sulphoxamide* (Laurent),  $\text{C}^2\text{N}^2\text{H}^4\text{S}^2 = \text{Cy}^2.2\text{H}^2\text{S}$ .—This compound, which has the composition of oxamide in which the oxygen is replaced by sulphur, is prepared by passing cyanogen gas and excess of sulphydic acid simultaneously into water, or better, into alcohol. The liquid gradually acquires a yellow-red colour, and deposits small crystals of the compound, which may be recrystallised from alcohol. It forms yellow-red shining opaque crystals very slightly soluble in cold water, somewhat more in boiling water, also in alcohol and ether. Strong sulphuric acid dissolves it with yellow colour, and deposits it again unaltered on addition of water. When it is gently heated, a small portion sublimates unaltered, the rest being resolved into sulphide of ammonium



and free carbon. It dissolves without alteration in cold potash; but when boiled with dilute potash, it yields oxalate and sulphide of potassium, together with ammonia:



A similar decomposition takes place when the compound is boiled with hydrochloric acid. Boiled with strong potash-solution it yields cyanide, sulphocyanate, and sulphide of potassium:



The compound is not decomposed by dry hydrochloric acid, or by sulphurous acid or ammonia either dry or aqueous. Chlorine decomposes it with aid of heat, forming chloride of sulphur; with boiling nitric acid, it forms sulphuric acid. The aqueous solution, mixed with nitrate of silver, gives off cyanogen and throws down sulphide of silver. With neutral acetate of lead, it yields an orange-yellow precipitate  $\text{C}^{\text{N}}\text{H}^{\text{Pb}}\text{S}$ , which retains its colour when carefully dried, but yields sulphide of lead when boiled with water (Wöhler, Völkkel). With cupric salts it yields a black-green precipitate which resembles the lead-salt in its reactions. With mercuric chloride it forms a thick white precipitate, and gives off hydrochloric acid. (Wöhler.)

(For further details respecting these compounds, see *Gmelin's Handbook*, viii. 116.)

**CYANOGEN, SULPHIDE OF.** See SULPHOCYANIC ANHYDRIDE.

**CYANOIL.**  $\text{C}^{\text{H}}\text{NO}$ ? (Rossignon, *Compt. rend.* xiii. 551.)—A volatile oil produced by the fermentation of pressed almond-cake and of many stone-fruits containing prussic acid. To prepare it, the bruised and moistened almond-cake is spread out on paper till the mass begins to ferment; the fermented mass is carefully distilled; and the distillate, which at first contains a small quantity of acetic acid, is collected in a receiver containing potash-ley. The cyanoil, which floats on the liquid in oily drops, is first treated with chlorine, and then rectified over potash. Cyanoil may also be obtained by fermenting almond-cake with cheese.

Cyanoil is a colourless, oily liquid which smells like bitter almonds, tastes somewhat sharp and astringent, is insoluble in water, and has a specific gravity of 1.009; it burns with a purple-red flame. When exposed to the air, it slowly volatilises without alteration. It is said not to be decomposed by potash, chlorine, bromine, or iodine. It mixes in all proportions with nitric acid, and dissolves camphor, naphthalin, and wax. It is said to contain 69.42 per cent. carbon, 10.54 hydrogen, 13.02 nitrogen, and 7.02 oxygen, numbers which may be represented by the empirical formula above given; but the investigation of this substance is altogether very imperfect.

**CYANOLITE.** A hydrated silicate of calcium occurring, intergrown with cerinite and centrallassite, in a kidney-shaped mass in the trap of Fundy Bay, a mile to the east of Black Rock, and forming the innermost portion of the mass. It is amorphous, with a fracture varying from flat conchoidal to even. Colour bluish grey; iridescent; opaque in the mass, translucent at the edges. Specific gravity = 2.495. Hardness = 4.5. Soluble in hydrochloric acid, with separation of gelatinous silica. Before the blowpipe it melts on the thin edges, forms clear beads with soda and borax, and a translucent glass with phosphorus-salt.

The analysis gave:

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{K}_2\text{O}$	$\text{H}_2\text{O}$
72.52	1.24	18.19	trace	0.61	6.91 = 99.47;

agreeing nearly with the formula  $14\text{CaO} \cdot 10\text{SiO}_2 + 5\text{H}_2\text{O}$  or  $14\text{CaO} \cdot 0.5\text{SiO}_2 + 5\text{H}_2\text{O}$ . (How, *Edinb. N. Phil. J.* x. 847.)

**CYANOSITE**, or *Cyanose*. Native sulphate of copper. (See SULPHATES.)

**CYANOTOLUIDINE.** Syn. with CYANOGENYLAMINE. (See BENZYLAMINE.)

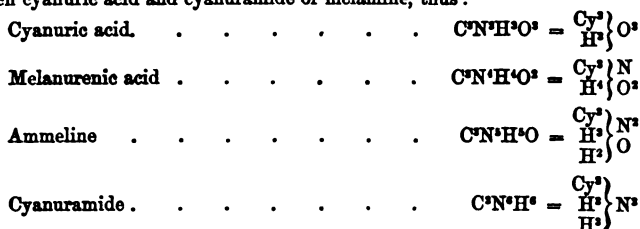
**CYANOTRICHITE.** *Lettsonite*, *Sammlerz*, *Kupfersammlerz*.—A mineral from Moldawa, in the Bannat, occurring in velvety deposits, consisting of delicate smalt-blue fibres. Two specimens analysed by Percy (*Phil. Mag.* [3] xxxv. 100) gave:

$\text{SO}^{\text{S}}$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{Cu}_2\text{O}$	$\text{H}_2\text{O}$	
15.38			48.16	23.06	= 98.30
14.12	11.06	1.18	46.59	23.06 insol.	2.35 = 98.36

whence the formula,  $6\text{Cu}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SO}^{\text{S}} + 12\text{H}_2\text{O} = \frac{12\text{Cu}^{\text{S}}}{2\text{Al}^{\text{III}}} \left\{ \text{O}^{\text{II}} + 12\text{aq.} \right.$   
 $\left. 2(\text{SO}^{\text{S}})^{\text{II}} \right\}$

**CYANOUS ACID.** The name originally given by Serullas to cyanic acid, on the supposition that it contained only half as much oxygen as the acid then called *cyanic*, but now *cyanuric acid*.

**CYANURAMIC ACIDS.** *Ammeline*,  $C^3N^3H^3O$ , and *Melanurenic acid*,  $C^3N^3H^3O^2$ , may be regarded as amic acids of cyanuric acid, both being intermediate in composition between cyanuric acid and cyanuramide or melamine, thus:



*Ammeline*,  $C^3N^3H^3O$ . (Liebig, Ann. Ch. Pharm. x. 30; lviii. 249. Knapp, *ibid.* xxi. 244. Laurent and Gerhardt, Ann. Ch. Phys. [3] xix. 92.)—This compound, which may also be regarded as composed of 2 at. cyanamide and 1 at. cyanic acid,  $2CyH^2N.CyHO$ , is produced by boiling melam with dilute sulphuric acid or potash-ley, or by boiling melamine (cyanuramide) with dilute nitric acid. It is precipitated from its solutions by ammonia or carbonate of potassium, as a chalky white powder. It is insoluble in water, alcohol, and ether, but dissolves in caustic alkalis and in most acids. Strong acids and alkalis convert it, first into ammelide, then into cyanuric acid. When heated it gives off ammonia and leaves mellone. Fused with potash, it yields cyanate of potassium (p. 193).

Ammeline is a weak base, forming crystalline salts, which are partially decomposed by water. The *nitrate*,  $C^3N^3H^3O.HNO^2$ , crystallises from solutions containing a slight excess of nitric acid, in long colourless four-sided prisms. When heated in the dry state, it gives off nitric acid and nitrate of ammonia—or the products of its decomposition, nitrous oxide and water—and leaves melanurenic acid:



The *argento-nitrate*,  $C^3N^3H^3O.AgNO^2$ , obtained by mixing a solution of nitrate of ammeline with nitrate of silver, is a white crystalline precipitate.

*Melanurenic acid*,  $C^3N^3H^3O^2 = CyH^2N.2CyHO$ . (Liebig and Wöhler, Ann. Ch. Pharm. liv. 371.—Gm. ix. 470.)—This body remains, together with cyanuric acid, when urea is subjected to a continuous but moderate heat. On dissolving out the cyanuric acid with water, the melanurenic acid remains as a white chalky powder, insoluble in water, soluble in acids and alkalis, and precipitable therefrom by neutralisation. When heated, it yields ammonia and mellone; and when boiled with acids or alkalis, it gives up ammonia and is converted into cyanuric acid.

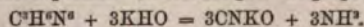
*Ammelide*,  $C^3N^3H^3O^2 = 3(CyH^2N.CyHO) = \frac{Cy^4}{H^3} \left\{ N^2 \right.$  (Liebig, Ann. Pharm. x. 30; lviii. 249. Knapp, *ibid.* lxix. 244. Laurent and Gerhardt, Ann. Ch. Phys. [3] xix. 94.)—This body, discovered by Liebig in 1834, stands, according to the above formula, intermediate between ammeline and melanurenic acid, just as ammeline does between melamine (cyanuramide) and melanurenic acid, and as melanurenic acid does between ammeline and cyanuric acid (see table above). Gerhardt, however (*Traité*, iv. 888), regards it identical with melanurenic acid. It is obtained by dissolving melam, melamine, or ammeline in nitric, or better, in strong sulphuric acid, and precipitating with alcohol or carbonate of potassium. It is a white powder, insoluble in water, soluble in acids, but does not form definite salts. It dissolves easily in dilute potash, and in boiling aqueous ammonia; and when the latter solution, freed from excess of ammonia by heat, is mixed with nitrate of silver, a precipitate of *ammelide of silver* is formed, consisting of  $C^3N^3H^3AgO^2$ .

A solution of this salt in strong nitric acid deposits colourless laminae or tables of *argento-nitrate of ammelide*,  $C^3N^3H^3O^2.AgNO^2$ . The same compound is obtained on mixing a cold saturated solution of ammelide in nitric acid with a solution of nitrate of silver not containing ammonia. The crystals treated with water dissolve, for the most part, leaving white flakes of ammelide. Heated in a tube, it first gives off nitrous vapours, then cyanic acid, and leaves metallic silver.

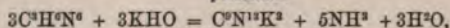
Ammelide boiled for some time with acids or alkalis is converted into cyanuric acid, and when fused with potash, yields cyanate of potassium.

**CYANURAMIDE.** *Tricyano-triamide*, *Melamine*.  $C^3H^3N^3 = \frac{Cy^3}{H^3} \left\{ N^3 \right.$  (Liebig, Ann. Ch. Pharm. x. 18; xxvi. 187.)—This compound, polymeric with cyanamide,

is obtained by heating the latter to  $150^{\circ}\text{C}$ ., or by boiling melam ( $\text{C}^3\text{H}^3\text{N}^3$ ) with potash and slowly evaporating the solution. It crystallises in large rhombic octahedrons, having a strong lustre, permanent in the air, slightly soluble in cold water, more soluble in boiling water, insoluble in alcohol and ether; boiling potash-ley dissolves them more readily than water. When strongly heated, they melt, give off ammonia, and leave an orange-yellow residue of hydromellone, which is further decomposed at a higher temperature. Cyanuramide, fused with *hydrate of potassium*, yields cyanate or mellonide of potassium, according to the proportions used:

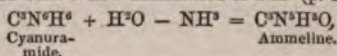


Cyanate of  
potassium.



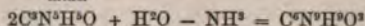
Mellonide of  
potassium.

When fused with *potassium*, it glows, gives off ammonia, and yields mellonide of potassium. Strong acids transform cyanuramide successively into ammeline, ammelide, melanurenic acid, and cyanuric acid, each of these compounds being derived from the preceding by the addition of  $\text{H}^2\text{O}$  and elimination of  $\text{NH}^3$  (p. 286).



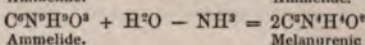
Cyanura-  
mide.

Ammeline.



Ammeline.

Ammelide.



Ammelide.

Melanurenic  
acid.



Melanurenic  
acid.

Cyanuric  
acid.

Cyanuramide, or melamine, is a base which unites easily with acids, forming well defined salts which have an acid reaction. Its aqueous solution precipitates the salts of manganese, iron, zinc, and copper.

*Acetate of melamine* is very soluble in water, and crystallises in large rectangular flexible tables. The *formate* forms very soluble laminae. The *nitrate*,  $\text{C}^3\text{H}^3\text{N}^3\cdot\text{HNO}^3$ , crystallises in long silky laminae, which are permanent in the air and may be recrystallised without decomposition. An *argentonitrate*,  $\text{C}^3\text{H}^3\text{N}^3\cdot\text{AgNO}^3$ , is produced on adding a hot solution of melamine to nitrate of silver, as a white crystalline precipitate, which increases on cooling, and may be recrystallised without alteration. The *oxalate*,  $\text{C}^2\text{H}^2(\text{C}^3\text{H}^3\text{N}^3)^2\text{O}^4$ , is less soluble in water than the nitrate. The *phosphate* forms slender needles very soluble in boiling water. The *sulphate* is a crystalline precipitate obtained by adding sulphuric acid to a solution of melamine. It is slightly soluble in cold water, more soluble in boiling water, and crystallises on cooling in short red needles.

**CYANURIC ACID.**  $\text{C}^3\text{H}^3\text{N}^3\text{O}^3 = \begin{matrix} \text{Cy}^3 \\ \text{H}^3 \end{matrix} \text{O}^3 = \left( \begin{matrix} \text{CO}^2 \\ \text{H}^2 \end{matrix} \right)^3 \text{N}^3$ . *Tricarbonyl-triamide*, *Cyanurenic acid*, *Pyro-uric acid*. (Scheele, *Opuscula*, ii. 177. Serullas, *Ann. Ch. Phys.* [2] xxxviii. 379. Wöhler, *Pogg. Ann.* xv. 622; *Ann. Ch. Pharm.* lxii. 241. Liebig and Wöhler, *Pogg. Ann.* xx. 369; xxiv. 508, 603. Liebig, *Ann. Ch. Pharm.* xxvi. 121, 125. Wurtz, *ibid.* lxiv. 307. De Vry, *ibid.* lxi. 248. Limpricht, *ibid.* lxxiv. 208.)

This acid was discovered by Scheele, who obtained it as a sublimate by the dry distillation of uric acid, and regarded it as similar to succinic acid. Serullas, in 1828, by decomposing solid chloride of cyanogen with water, obtained an acid which he regarded as  $\text{C}^2\text{NHO}^2$ , and named cyanic acid (p. 286); and Wöhler, in 1829, showed that this acid was identical with pyro-uric acid, and was also obtained as a residue by heating urea. Subsequently, Liebig and Wöhler, in 1830, discovered the true composition of the acid and many of its chemical relations.

Cyanuric acid is also produced: *a.* By heating urea to a certain point (Wöhler, *Gm.* vii. 366).—*b.* In the decomposition of urea by hydrochloric acid (De Vry), or by chlorine (Wurtz).—*c.* By boiling melamine with nitric acid, or cyanic acid with sulphuric acid (Liebig).—*d.* By boiling 1 pt. of ammelide for six hours with 50 pts. of water and a quantity of phosphoric, sulphuric, or nitric acid, about sufficient to dissolve the ammelide, the ebullition being continued till the liquid is no longer precipitated by ammonia.—*e.* By boiling 1 pt. of ammelide for an hour with 10 pts. of dilute potash (Knapp, *Ann. Ch. Pharm.* xxi. 245).—*f.* By the action of aqueous hypochlorous acid on hydrocyanic acid. (Balard.)

*Preparation.*—1. Dry chlorine gas is passed into melting urea, whereupon the mass



swells up strongly, gives off white fumes of sal-ammoniac, together with nitrogen and hydrochloric acid, and is converted into cyanuric acid. (Wurtz.)



2. Urea is heated till it ceases to give off ammonia, the residue is dissolved in boiling water, and the filtrate is left to crystallise by cooling (Wöhler). As the urea-residue may still contain ammonia and still exhibit colour, it must be dissolved in hot sulphuric acid, nitric acid dropped into the solution till all effervescence ceases and the solution is decolorised, and after cooling, the cyanuric acid precipitated from it by water; it is then obtained as a snow-white crystalline powder; or it may be dissolved in boiling hydrochloric acid, which will deposit the cyanuric acid as it cools; or the pulverised residue may be suspended in water, and chlorine passed through the liquid, whereupon the residue dissolves, forming a solution which deposits cyanuric acid in proportion as the chlorine escapes. (Wöhler and Liebig.)

3. Pulverised urea is saturated with dry hydrochloric acid gas; the compound is heated in the oil-bath to  $145^{\circ}\text{C}$ ., at which temperature it begins to decompose, then taken out, whereupon violent decomposition takes place, and the temperature of the mass rises to  $200^{\circ}$ ; and the residue is dissolved in hot water, which on cooling deposits white cyanuric acid, whilst sal-ammoniac remains in the solution. If the mass were left in the oil-bath, the compound  $\text{C}^{\text{N}}\text{N}^{\text{H}}\text{O}^{\text{N}}$  would be obtained instead of cyanuric acid. (De Vry.)

4. Solid chloride of cyanogen is boiled with a large quantity of water in a flask provided with a long neck, that which sublimes in the neck being continually returned to the liquid by agitation, till the odour of chloride of cyanogen is no longer perceptible. The liquid is then placed in a basin and evaporated nearly to dryness at a gentle heat, the greater part of the hydrochloric acid escaping; the crystallised cyanuric acid is washed on a filter with small quantities of cold water till the water gives, with nitrate of silver, only a slight precipitate which dissolves in nitric acid; the acid is then dissolved in boiling water, and the filtrate evaporated to a certain point, and left to crystallise. (Serullas.)

*Properties.*—Cyanuric acid crystallises from water in colourless oblique rhombic prisms containing 2 at. water of crystallisation:  $\text{C}^{\text{N}}\text{N}^{\text{H}}\text{O}^{\text{N}} + 2\text{H}^{\text{O}}$ . The finest crystals are obtained by saturating a solution at the boiling heat, evaporating it at  $60^{\circ}$ – $80^{\circ}\text{C}$ ., and leaving it to cool slowly. According to Keferstein (Pogg. Ann. xcix. 275) and Schabus (*Bestimmung*, p. 142), the crystals are monoclinic, exhibiting the faces  $\infty\text{P}$ .  $\infty\text{P}\infty$ .  $\text{oP}$ .  $-\text{P}\infty$ .  $-\frac{1}{2}\text{P}\infty$ . Ratio of axes  $a : b : c = 0.5728 : 0.7526 : 1$ . Inclination of  $\infty\text{P}$  :  $\infty\text{P}$  in the clinodiagonal principal section =  $76^{\circ} 48'$  ( $77^{\circ} 13'$  Keferstein);  $\text{oP}$  :  $\infty\text{P} = 99^{\circ} 59'$ ;  $\text{oP}$  :  $-\text{P}\infty = 137^{\circ} 3'$ ;  $\text{oP}$  :  $-\frac{1}{2}\text{P}\infty = 161^{\circ} 42'$ . Cleavage very distinct parallel to  $-\text{P}\infty$ ; less distinct parallel to  $\text{oP}$ .

The crystals, exposed to dry air or gently heated, give off their water of crystallisation, amounting to 21.69 per cent., and leave anhydrous cyanuric acid in the form of a white efflorescent mass. The anhydrous acid likewise separates from a hot saturated solution of the acid in nitric or hydrochloric acid. By sublimation it is obtained in delicate needles.

Cyanuric acid is inodorous, has a slightly acid taste, and reddens litmus faintly. It is not poisonous. It is but slightly soluble in cold water (in 40 pts. according to Chevallier and Lassaigue), dissolves in 24 pts. of boiling water, and is insoluble in alcohol.

*Decompositions.*—1. Cyanuric acid when heated alone is converted into cyanic acid ( $\text{C}^{\text{N}}\text{N}^{\text{H}}\text{O}^{\text{N}} = 3\text{CNHO}$ ), part of the latter being at the same time converted into cyanelide (p. 186) which sublimes (Liebig and Wöhler). When mixed with nitrate of ammonia, it undergoes this change at a lower temperature than when heated alone (Pelouze, Ann. Ch. Phys. [3] vi. 69).—2. By prolonged boiling with nitric or hydrochloric acid, it is resolved into ammonia and carbonic acid (Liebig).—3. Heated with six times its weight of pentachloride of phosphorus, it yields solid chloride of cyanogen and oxychloride of phosphorus (Beilstein, p. 181).—4. Heated with potassium, it yields cyanide and hydrate of potassium,  $\text{C}^{\text{N}}\text{N}^{\text{H}}\text{O}^{\text{N}} + \text{K}^{\text{N}} = 3\text{CNK} + 3\text{KHO}$ . (Serullas.)

*Cyanurates.* Cyanuric acid is tribasic, being the analogue of solid chloride of cyanogen. It forms neutral salts,  $\text{Cy}^{\text{N}}\text{M}^{\text{O}}\text{O}^{\text{N}}$ , of which, however, only the lead and silver salts have been obtained, and acid salts containing 2 at. and 1 at. metal in place of hydrogen, viz.  $\text{Cy}^{\text{N}}\text{HM}^{\text{O}}\text{O}^{\text{N}}$  and  $\text{Cy}^{\text{N}}\text{H}^{\text{N}}\text{MO}^{\text{N}}$ . All the cyanates appear to be crystallisable, even those which are obtained by precipitation appearing crystalline under the microscope. They are decomposed by hydrochloric and nitric acid, with separation of cyanuric acid. The cyanurates of the alkali-metals when heated give off cyanic acid, cyanate of ammonium, carbonic anhydride, and nitrogen, and leave a

residue of cyanate. They are easily soluble in water; the other cyanurates are insoluble, or sparingly soluble.

*Cyanurate of Ammonium*,  $\text{Cy}^3\text{H}^2(\text{NH}^1)\text{O}^3 + \text{aq.}$  (dried in vacuo).—White shining prisms which effloresce in contact with the air, and give off ammonia when heated. They are but slightly soluble in water, the solution smelling of ammonia.

*Cyanurate of Barium*.—The *monobarytic salt*,  $\text{Cy}^3\text{H}^2\text{BaO}^3 + \text{aq.}$ , is produced by dropping baryta-water into a boiling solution of the acid as long as the resulting precipitate redissolves. The salt, which is nearly insoluble, gradually separates in small shining prisms. It begins to give off water at  $200^\circ\text{C.}$ , and becomes anhydrous and milk-white at  $280^\circ$ .

The *tribarytic salt*,  $\text{Cy}^3\text{HBa}^2\text{O}^3 + \text{aq.}$ , is obtained, on pouring a hot solution of the acid into an excess of baryta-water, as a pulverulent precipitate composed of microscopic crystals. It is likewise produced on mixing a boiling solution of the acid with chloride of barium and adding ammonia. The free acid does not precipitate either chloride or acetate of barium. At  $200^\circ\text{C.}$  it begins to give off water of crystallisation (amounting to 6·3 per cent.), and at a higher temperature, gives off ammonia, then cyanic acid, and leaves fused cyanate of barium.

*Cyanurate of Calcium* crystallises in nodules. It is easily soluble in water; has a sharp, bitter taste; melts at a gentle heat, and solidifies on cooling in a yellowish waxy mass. It contains 8·6 per cent. lime. (Chevallier and Lassaigue, Ann. Ch. Phys. xiii. 155.)

*Cyanurate of Copper*.—A definite salt appears difficult to obtain.—*a.* Recently precipitated cupric hydrate added by small portions to hot aqueous cyanuric acid till the liquid is saturated, forms a clear solution, and, on cooling, soon yields a bluish-green crystalline precipitate, which assumes a fine blue colour at  $100^\circ\text{C.}$ , and at  $250^\circ$  gives off 9 per cent. water, and changes to pure green just like chromic oxide; it appears to be a basic salt with more than 3 at. copper.—*b.* Crystallised cyanurate of ammonium dissolved in water, forms with cupric sulphate a greenish-blue amorphous precipitate, which when heated becomes crystalline and assumes, first, a blue, then a green colour; it is free from ammonia, but contains sulphuric acid as an essential constituent. The liquid filtered from this precipitate deposits crystallised cyanuric acid.—*c.* When aqueous solutions of cyanuric acid and cupric acetate saturated while hot, are boiled together for some time, a green precipitate is formed containing acetic acid in combination. (Wöhler.)

*Cyanurate of Cuprammonium*,  $\text{Cy}^3\text{H}(\text{NH}^2\text{Cu})^2\text{O}^3 + \text{aq.}$ —A solution of cyanuric acid in very dilute ammonia, mixed while hot with a solution of cupric sulphate in very dilute ammonia, deposits, on cooling, crystals which may be washed with water, inasmuch as they dissolve in it but sparingly. The salt forms small amethyst-coloured crystals, which, when examined by the microscope, appear to be four-sided prisms, with two of the lateral faces broader than the others, and bevelled with two faces. It is permanent in the air, begins to give off ammonia at  $100^\circ\text{C.}$ , and at  $230^\circ$  assumes a dark-olive green colour, with loss of 14·85 per cent. At a still higher temperature it suddenly becomes yellow, then takes fire, and glimmers away till it is converted into cupric oxide.

If in the preparation of this salt, the ammonia is not used in too great excess, and the liquids are mixed at the boiling heat, a beautiful peachblossom-coloured crystalline precipitate is formed, which is likewise an ammonio-cupric salt. It dissolves in ammonia, forming an azure-blue solution which soon begins to deposit small crystals having a smalt-blue colour, but changing into the peach-blossom-coloured salt on exposure to the air, from loss of ammonia.

*Cyanurates of Copper and Ammonium*.—The dark-green salt obtained, as above mentioned, by heating cyanurate of cuprammonium to  $230^\circ\text{C.}$ , contains, according to Wöhler,  $\text{Cy}^3\text{Cu}^2(\text{NH}^1)\text{O}^3 + \frac{1}{2}\text{aq.}$ ; according to Gerhardt and Gmelin,  $\text{Cy}^3\text{Cu}^2(\text{NH}^1)\text{O}^3$ . Wiedemann (Pogg. Ann. lxxiv. 73), by adding a solution of cyanuric acid in excess of ammonia to an ammoniacal solution of cupric sulphate, obtained a violet precipitate of the salt,  $\text{Cy}^3\text{HCu}(\text{NH}^1)\text{O}^3$ , insoluble in cold water, and sparingly soluble in ammonia.

*Cyanurate of Ethyl*. See CYANURIC ETHERS.

*Cyanurate of Lead*,  $\text{Cy}^3\text{PbO}^3 + \text{aq.}$ , is produced when a boiling solution of cyanuric acid is mixed with a hot solution of neutral, or better, of basic acetate of lead, the salt then separating after a few seconds in the form of a pulverulent precipitate. It is also produced when recently precipitated carbonate of lead is boiled with a large excess of cyanuric acid. In the mass, it exhibits a pale yellowish colour. Under a strong magnifier, it is seen to consist of transparent prisms with obliquely set terminal faces, often united in twins or in fern-like groups. It begins to give off water

at 240° C.; but the last portions do not go off till the salt is raised to a higher temperature, at which also ammonia begins to escape. When still more strongly heated, it leaves pure protoxide of lead; when heated in a stream of hydrogen, it leaves metallic lead, a large quantity of cyanide of ammonium being formed at the same time together with urea. (Wöhler.)

*Cyanurate of Methyl.* }  
*Cyanurate of Phenyl.* } See CYANURIC ETHERS.

*Cyanurates of Potassium.*—The *monopotassic salt*,  $\text{Cy}^{\text{H}}\text{K}^{\text{O}}$ , is obtained by mixing a boiling saturated solution of cyanuric acid with a quantity of potash not sufficient for complete neutralisation: it is then deposited in shining cubes. It is also precipitated on adding acetic or nitric acid by small portions to a strong aqueous solution of cyanate of potassium. Campbell (Ann. Ch. Pharm. xxviii. 52) prepares it by roasting ferrocyanide of potassium in an open vessel, digesting the product with a small quantity of water, precipitating the cold solution with hydrochloric acid, and crystallising the precipitated cyanurate from boiling water. It is sparingly soluble in water, and the solution has an acid reaction. 1 at. of this salt ignited with 2 at. hydrate of potassium, yields 3 at. cyanate:  $\text{Cy}^{\text{H}}\text{K}^{\text{O}} + 2\text{KHO} = 3\text{CyKO} + 2\text{H}^{\text{O}}$  (Liebig). The crystals, when fused, are resolved, without blackening, into cyanate of potassium and cyanic acid vapour, which condenses as cyamelide:  $\text{Cy}^{\text{H}}\text{K}^{\text{O}} = \text{CyKO} + 2\text{CyHO}$ . (Liebig and Wöhler.)

The *dipotassic salt*,  $\text{Cy}^{\text{H}}\text{K}^{\text{O}}$ , is precipitated on adding alcohol to a solution of the preceding salt in caustic potash. It crystallises in white needles: its solution has an acid reaction, and decomposes after some time into potash and monopotassic cyanurate. Acetic acid added to the solution also throws down the monopotassic salt, so likewise does a small quantity of nitric acid, but a larger quantity precipitates cyanuric acid. The dipotassic salt is decomposed by heat, like the monopotassic salt, into cyamelide and cyanate of potassium:  $\text{Cy}^{\text{H}}\text{K}^{\text{O}} = 2\text{CyKO} + \text{CyH}^{\text{O}}$ . (Liebig and Wöhler.)

*Cyanurates of Silver.*—The *diargentate salt*,  $\text{Cy}^{\text{H}}\text{Ag}^{\text{O}}$ , is obtained:—1. By adding recently precipitated carbonate of silver to a boiling solution of cyanuric acid, in such proportion as not to saturate it completely.—2. By mixing a boiling solution of cyanuric acid with acetate of sodium, and adding this mixture drop by drop to a dilute boiling solution of nitrate of silver, in such proportion as to leave the latter in excess—otherwise the precipitate will be mixed with an insoluble double cyanurate of silver and sodium.—3. By adding a solution of cyanurate of ammonium drop by drop to a boiling solution of nitrate of silver, the latter being kept in excess.—4. By mixing a hot solution of acetate of silver with a boiling solution of cyanuric acid. This last process yields the purest product. The presence of free acetic acid in the solution of the silver-salt does not interfere with the result, as cyanurate of silver is not decomposed by acetic acid, even when concentrated; but it is completely decomposed by dilute nitric acid, and is consequently not precipitated on adding cyanuric acid to nitrate of silver.

Diargentate cyanurate is colourless, crystalline, insoluble in water, and blackens when exposed to light. When examined by the microscope, it appears to be composed of transparent rhombohedrons. At 200° C. it neither loses weight nor changes colour; at a higher temperature, it acquires a cinnamon colour, but does not diminish in weight by more than a few thousandths. At a still stronger heat, it emits a strong odour of cyanic acid, acquires a deep violet colour, and finally leaves a residue of metallic silver. In an atmosphere of hydrogen, it is reduced to an argentous salt, even at 100° C. It dissolves in nitric acid, but is decomposed at the same time, yielding free cyanuric acid. (Wöhler.)

The *triargentate salt*,  $\text{Cy}^{\text{H}}\text{Ag}^{\text{O}}$ , is obtained by adding nitrate of silver to a boiling solution of cyanuric acid in excess of ammonia, boiling the precipitate with the liquid for a quarter of an hour, then filtering, and washing with hot water. (Liebig.)

It is snow-white, and does not blacken when exposed to light; the microscope shows it to consist of small prisms. It is insoluble in water, very slightly soluble in dilute nitric acid. When dried at 100° C. it retains  $1\frac{1}{2}$  at. water ( $2\text{Cy}^{\text{H}}\text{Ag}^{\text{O}} + \text{aq.}$ ), which it appears to retain till heated to 300° C. The anhydrous salt absorbs water greedily from the air.

According to Wöhler, the salt gives off ammonia when heated, partly below 100° C., but the greater part between 100° and 300° C.; also when digested with potash; hence Wöhler supposes that the precipitated salt consists of  $\text{Cy}^{\text{H}}\text{Ag}^{\text{O}}\cdot\text{NH}^{\text{H}} + \frac{1}{2}\text{aq.}$  According to Debus, however, potash does not eliminate ammonia from it, except at a very high temperature.

*Cyanurate of Argentammonium*,  $\text{Cy}^{\text{H}}(\text{NH}^{\text{H}}\text{Ag})^{\text{O}}$ , is obtained by digesting diargentate cyanurate with caustic ammonia, whereby it is altered in appearance, but does



not dissolve. The product begins to give off ammonia at 60° C., and between 200° and 300°, is completely reduced to diargentate cyanurate.

*Cyanurates of Silver and Ammonium.*—The liquid filtered from the precipitate of triargentate cyanurate obtained as above, deposits, on cooling, a white powder consisting of  $\text{Cy}^{\text{a}} \left\{ \begin{smallmatrix} \text{NH}^{\text{a}} \\ \text{Ag}^{\text{a}} \end{smallmatrix} \right\} \text{O}^{\text{a}} + \text{H}^{\text{a}}\text{O}$ , which may be washed and dried at the temperature of the air.\* The same salt is obtained by boiling together the solutions of nitrate of silver and cyanurate of ammonium. It crystallises in very slender microscopic prisms. It gives off ammonia when treated with potash, also when heated to a temperature below 100° C. Heated for two hours to 250° C., it gives off ammonia and water, and leaves the salt  $\text{Cy}^{\text{a}} [\text{H}^{\text{a}} (\text{NH}^{\text{a}}) \text{Ag}^{\text{a}}] \text{O}^{\text{a}}$ , which, at a stronger heat, assumes a violet colour and fumes strongly. Wöhler likewise obtained another salt, which, after drying over sulphuric acid, contained 41.4 p. c. silver. It was soluble in hot dilute ammonia, and separated therefrom on cooling.

*Cyanurate of Silver and Lead.*  $\text{Cy}^{\text{a}} \text{Ag}^{\text{a}} \text{PbO}^{\text{a}} + \text{aq.}$ —When cyanurate of lead is boiled with a large excess of nitrate of silver, till its appearance is quite altered, a filtrate is obtained, containing a large proportion of lead, the double salt remaining on the filter. The latter, after drying at 100° C., yields, when reduced by hydrogen, 69.64 p. c. of an alloy consisting of 45.94 p. c. silver, and 23.70 lead. (Wöhler.)

*Cyanurate of Silver and Potassium.*—Diargentate cyanurate boiled with caustic potash is not decomposed, but takes up potassium, forming a double salt which melts and decomposes when heated, leaving a residue of cyanate and carbonate of potassium, together with 60 p. c. silver. The salt  $\text{Cy}^{\text{a}} \text{Ag}^{\text{a}} \text{K}^{\text{a}} \text{O}^{\text{a}}$  should leave 55 p. c. silver: the product probably contained unaltered diargentate cyanurate. (Wöhler.)

*Cyanurate of Sodium.*—Uncrystallisable, very soluble in water.

*Cyanurate of Urea!*—By dissolving cyanuric acid in a boiling saturated solution of urea, and cooling the liquid, delicate needles are obtained. (Kodweiss, Pogg. Ann. xix. 11.)

**CYANURIC ETHERS.** (Wurtz, Compt. rend. xxvi. 368; xxvii. 341; Ann. Ch. Phys. [3] xlii. 43; l. 120. Limpricht, Ann. Ch. Pharm. lxxiv. 208. Limpricht and Habich, *ibid.* cv. 395. Gerhardt, Compt. chim. 1850, p. 391.)—Three of these compounds are known, analogous in composition to the trimetallic cyanurates, and one analogous to the dimetallic cyanurates. They are crystalline solids which distil without decomposition, and react with alkalis in the same manner as the cyanic ethers, yielding an alkaline carbonate and an amine.

**CYANURATES OF ETHYL.**—*a. Triethylic Cyanurate. Neutral Cyanuric ether,*

$\text{C}^{\text{a}} \text{N}^{\text{a}} \text{H}^{\text{a}} \text{O}^{\text{a}} = \left\{ \begin{smallmatrix} \text{Cy}^{\text{a}} \\ \text{C}^{\text{a}} \text{H}^{\text{a}} \end{smallmatrix} \right\} \text{O}^{\text{a}}$ , or *Triethyl-tricarbonyl-triamide*,  $\text{N}^{\text{a}} \left\{ \begin{smallmatrix} (\text{C}^{\text{a}} \text{O})^{\text{a}} \\ \text{C}^{\text{a}} \text{H}^{\text{a}} \end{smallmatrix} \right\}$ .—This compound, discovered by Wurtz, is obtained by distilling a mixture of ethylsulphate and cyanate or cyanurate of potassium; or by heating cyanate of silver, either neutral or acid, with iodide of ethyl to 120° C., and lastly, by molecular transformation of the cyanate in contact with triethylphosphine. (Hofmann, Chem. Soc. Qu. J. xiii. 322.)

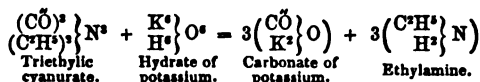
When a mixture of equal parts of ethylsulphate of potassium and dipotassic cyanurate (p. 291) is heated in a retort, cyanurate of ethyl distils over, together with carbonate of ammonium, ethylamine, cyanide of ethyl, and other secondary products, and condenses in the neck of the retort and in the receiver, as a crystalline mass, which may be purified by repeated crystallisation from dilute alcohol.—On distilling the ethylsulphate with cyanate of potassium, an acrid liquid distillate is obtained, consisting of cyanurate and cyanate of ethyl (p. 195). The latter, which is very volatile, may be distilled off at 60° C., and the crystalline cyanurate which remains may be purified by recrystallisation from alcohol. This process, according to Wurtz, is easier than the former.

Triethylic cyanurate crystallises in trimetric combinations,  $\infty \text{P} . \infty \tilde{\text{P}} \infty . \tilde{\text{P}} \infty$ . Inclination of  $\infty \text{P} : \infty \text{P} = 128^\circ$ ;  $\tilde{\text{P}} \infty : \tilde{\text{P}} \infty$  over the principal axis =  $93.5^\circ$ . Ratio of axes,  $a : b : c = 0.4877 : 1 : 0.9407$ . It melts at  $95^\circ \text{C.}$  to a colourless liquid heavier than water, volatilises easily with vapour of water, and boils without decomposition at  $235^\circ \text{C.}$  Vapour-density, obs. = 7.4; calc. (2 vol.) = 7.37. It is slightly soluble in water, easily in alcohol and ether. The solutions are perfectly neutral. From the cold alcoholic solution, it is precipitated in the crystalline form by water.

Triethylic cyanurate dissolves easily and without decomposition in acids, even in hot concentrated nitric acid. It is not altered by heating with pentachloride of phos-

\* Wöhler, regarding cyanuric acid as dibasic, gave for this salt the formula:  $3\text{AgO} . \text{C}^{\text{a}} \text{N}^{\text{a}} \text{HO}^{\text{a}} + 3\text{NH}^{\text{a}} \text{O} . \text{C}^{\text{a}} \text{N}^{\text{a}} \text{HO}^{\text{a}}$ , or  $\text{AgO} . \text{Cy}^{\text{a}} \text{Ag}^{\text{a}} \text{HO}^{\text{a}} + \text{NH}^{\text{a}} \text{O} . \text{Cy}^{\text{a}} (\text{NH}^{\text{a}})^{\text{a}} \text{HO}^{\text{a}}$ .

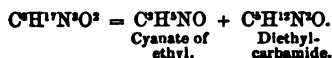
phorus. It is decomposed by boiling with *alkalis*, the ultimate products of the reaction being ethylamine and a carbonate of the alkali-metal:



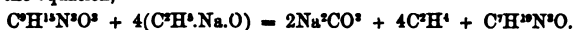
Intermediate products are, however, formed, which are obtained in the greatest degree of purity by heating the cyanuric ether with baryta-water. Carbonate of barium then separates, and on removing the excess of baryta from the solution by means of carbonic acid, there remains a liquid sparingly soluble in water, easily in alcohol and ether, and composed of  $\text{C}^{\text{H}}^{\text{H}}\text{N}^{\text{s}}\text{O}^{\text{s}}$ . (Limpricht and Habich.)



This body heated to  $170^{\circ}$ — $200^{\circ}$  C. is resolved into cyanate of ethyl and diethyl-carbamide, the latter distilling over at  $250^{\circ}$ .



Cyanurate (and sometimes also cyanate, p. 196) of ethyl, heated with dry *ethylate of sodium*, yields, together with ethylene, a distillate containing alcohol, ethylamine, and hydrate of triethyl-carbotriamine,  $\text{C}^{\text{H}}^{\text{H}}\text{N}^{\text{s}}\text{O}^{\text{s}} = \text{N}^{\text{s}}[\text{C}^{\text{H}}^{\text{s}}(\text{C}^{\text{H}}^{\text{s}})^{\text{s}}\text{H}^{\text{s}}]\text{H}^{\text{s}}\text{O}$  (Hoffmann, Compt. rend. lii. 1290). The formation of this compound may be represented by the equation,



The formation of Limpricht's compound,  $\text{C}^{\text{H}}^{\text{H}}\text{N}^{\text{s}}\text{O}^{\text{s}}$ , of hydrate of triethylcarbotriamine, and of ethylamine (3 at.) from triethylic cyanurate, may be supposed to take place by the successive subtraction of  $\text{CO}^{\text{s}}$  and addition of  $\text{H}^{\text{s}}\text{O}$ .

*Tetrachloro-triethylic Cyanurate*,  $\text{C}^{\text{H}}^{\text{H}}\text{Cl}^{\text{s}}\text{N}^{\text{s}}\text{O}^{\text{s}}$ , is produced, with elimination of hydrochloric acid, when triethylic cyanurate is heated to  $150^{\circ}$  C. in dry chlorine gas. It is a hard solid body, perfectly transparent, but rarely crystalline; melts to a mobile liquid when heated; and may be distilled without decomposition. Its alcoholic solution mixed with alcoholic potash, even in the cold, yields chloride and carbonate of potassium, together with the compound  $\text{C}^{\text{H}}^{\text{H}}\text{Cl}^{\text{s}}\text{N}^{\text{s}}\text{O}^{\text{s}}$ , which, when the excess of alcohol has been removed by evaporation, remains as a viscid mass. (Limpricht and Habich.)

*Diethylic Cyanurate, Diethylcyanuric acid, Cyanuric ether*,  $\text{C}^{\text{H}}^{\text{H}}\text{N}^{\text{s}}\text{O}^{\text{s}} =$

$\begin{array}{c} \text{Cy}^{\text{s}} \\ \text{H}(\text{C}^{\text{H}}^{\text{s}})^{\text{s}} \end{array} \left\{ \text{O}^{\text{s}} \right\}$ ; or *Diethyl-tricarbonyl-triamide*  $= \begin{array}{c} (\text{CO})^{\text{s}} \\ \text{H}(\text{C}^{\text{H}}^{\text{s}})^{\text{s}} \end{array} \left\{ \text{N}^{\text{s}} \right\}$ .—This compound is obtained, together with the preceding, by distilling a mixture of cyanurate and ethylsulphate of potassium. It passes over when the heat is raised, towards the end of the distillation, and remains in the mother-liquor after the triethylic cyanurate has crystallised out; but on evaporating this mother-liquor to dryness, boiling the residue with baryta-water as long as volatile bases are given off, removing the baryta with sulphuric acid, and leaving the filtrate to evaporate, the diethylic cyanurate separates in crystals (Limpricht).—Wurtz obtained this compound in the preparation of diethyl-carbamide.

Diethylic cyanurate crystallises from alcohol in rhombohedrons, or in six-sided prisms with rhombohedral summits. It melts at  $173^{\circ}$  C., and volatilises without decomposition at higher temperatures. It is easily soluble in *alcohol, ether*, and *hot water*, the aqueous solution having an acid reaction. It dissolves readily also in *alkalis*, but does not form definite salts with them. It does not alter in weight when immersed either in *ammonia* or in *hydrochloric acid gas*. When heated with *potash*, it gives off ethylamine and ammonia. *Baryta-water* decomposes it in like manner at a temperature above  $100^{\circ}$  C.

*Diethylcyanurate of Silver*,  $\text{C}^{\text{H}}^{\text{H}}\text{AgN}^{\text{s}}\text{O}^{\text{s}}$ , is precipitated in white needles on mixing an ammoniacal solution of the acid with nitrate of silver. *Diethyl-cyanurates of mercurous, cupricum, and lead*, are obtained in like manner. The lead-salt distilled with ethylsulphate of potassium, yields triethylic cyanurate. (Limpricht and Habich.)

CYANURATE OF METHYL,  $\text{C}^{\text{H}}^{\text{s}}\text{N}^{\text{s}}\text{O}^{\text{s}} = \begin{array}{c} \text{Cy}^{\text{s}} \\ (\text{CH}^{\text{s}})^{\text{s}} \end{array} \left\{ \text{O}^{\text{s}} \right\}$ , or *Trimethyl-tricarbonyltriamide*,

$\begin{array}{c} (\text{CO})^{\text{s}} \\ (\text{CH}^{\text{s}})^{\text{s}} \end{array} \left\{ \text{N}^{\text{s}} \right\}$ . Prepared, like triethylic cyanurate, by distilling methylsulphate of



potassium with cyanurate or cyanate of potassium, and purified by crystallisation from alcohol. It is likewise formed by molecular transformation of methylic cyanate when kept in sealed tubes. It forms small, colourless, opaque prisms, which melt at  $175^{\circ}$ — $176^{\circ}$  C., and boil at  $274^{\circ}$  (higher than the ethyl-compound). It is insoluble in cold water, slightly soluble in hot water, easily in alcohol. Vapour-density (obs.) = 5.98 (cal. 2 vol. = 5.94).—Boiled with *potash*, it yields methylamine. (Wurtz.)

**CYANURATE OF PHENYL**,  $C^6H^5N^3O^3 = Cy^3(C^6H^5)^3O^3$ . Produced by molecular transformation of the cyanate (p. 197), in contact with triethylphosphine. The mixture on cooling solidifies to a mass of shining crystals, which are insoluble in water, nearly insoluble in ether, and dissolve with difficulty in alcohol, even at the boiling heat. (Hofmann, Chem. Soc. Qu. J. xiii. 322.)

**CYANURIN**. This name is applied to a pathological blue deposit, sometimes found in urine (*q. v.*)

**CYANYL**. This name is applied by Boutin (Compt. rend. x. 452; xi. 820) to a product which he obtained, together with aloetic, chrysammic, and picric acids, by oxidising aloes with nitric acid. He describes it as a colourless liquid, smelling like prussic acid, insoluble in water, heavier than water, distilling without decomposition at a high temperature, and very poisonous.

**CYANYLIC ACID**.  $C^6N^3H^3O^3$ . (Liebig, Ann. Ch. Pharm. x. 32.) An acid isomeric with cyanuric acid. It is obtained by dissolving mellone in boiling nitric acid, either dilute or concentrated, leaving the solution to cool till it crystallises, freeing the crystals from nitric acid by cold water, and then recrystallising from hot water. Cyanuric acid is often mixed with the product, but always crystallises out first.

The acid crystallises in combination with water, in long, transparent, colourless, rhombic prisms, or in broad laminae having a pearly lustre.

The crystals effloresce when exposed to the air. The acid, like cyanuric acid, volatilises in the form of cyanic acid when heated.—By solution in strong sulphuric acid, and precipitation by water, it is converted into cyanuric acid, and no longer exhibits the pearly lustre above mentioned, after crystallisation from water. It dissolves in water somewhat more readily than cyanuric acid; and the hot saturated aqueous solution solidifies almost wholly in a laminated mass on cooling.

All the *Cyanylates*, *e. g.* those of the fixed alkali-metals and alkaline-earth-metals, are completely decomposed by the stronger acids, so that as the liquid cools, the cyanylic acid crystallises out in the free state.

Cyanylic acid neutralised with ammonia, forms with nitrate of silver a white, tumefied precipitate, which after drying is pulverulent, amorphous, and contains 45.36 per cent. of silver; but the precipitate obtained with cyanylate of potassium has the composition of cyanurate of silver, probably because the potash converts the cyanylic acid into cyanuric.

**CYCLAMEN EUROPEUM**. *Sow-bread*.—A small plant of the primulaceous order, forming flat round tubers, which, in addition to the ordinary constituents of plants, contain, according to Saladin, arthanitin (*i. 412*), according to De Luca, cyclamin and mannite. The juice of the tubers is harmless to most animals, though small fishes die when immersed in water containing only  $\frac{1}{2000}$  to  $\frac{1}{20000}$  of it; but when introduced into the blood it acts as a powerful poison, like curara, only not so strongly (Bernard); bromine is found to be an antidote to it, as well as to curara.

**CYCLAMIN**. A non-azotised glucoside, extracted from the tubers of *Cyclamen europæum*, and constituting the poisonous principle of that plant. Saladin (*J. Chim. med. vi. 417*) obtained from *Radices arthanita*, the officinal roots of *Cyclamen europæum*, an impure substance called arthanitin or cyclamin (*i. 412*), but the substance to which the latter name is now applied was first prepared by De Luca (*Cimento nuovo, v. 225; viii. 182*) and Martius (Buchner's N. Repert. [1859] viii. 388).

*Preparation*.—The tubers, cleansed and cut in pieces, are macerated for about six weeks with rather less than their own weight of rectified spirit, in the dark and in a cool place, then pressed; the residue again treated for about a month with a somewhat smaller quantity of alcohol; and the second residue again submitted to the same treatment. On filtering off the alcoholic liquid, a gelatinous substance remains, which is to be evaporated over the water-bath in the dark, and then exhausted with alcohol. The filtered solution left to evaporate in the dark, leaves cyclamin in small amorphous lumps, which may be washed with cold alcohol and dissolved in boiling alcohol; the solution on cooling deposits cyclamin.

*Properties*.—Cyclamin is a white, amorphous, neutral, inodorous substance, producing, after a short time, a very irritating sensation in the throat. It turns brown when exposed to light, absorbs water from moist air to the amount of about half its weight, and swells up. In contact with cold water, it is converted into a translucent glutinous



substance, which dissolves slowly, forming a liquid which has a slight optical laevorotatory power, froths when agitated, and coagulates like white of egg at 60°–75° C.; the coagulum redissolves when left for some days in the cold, and is reproduced on heating.

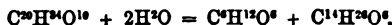
The formula of cyclamin is not yet fixed. De Luca deduces from his own analysis the empirical formula  $\text{C}^{20}\text{H}^{40}\text{O}$ ; Martius, from Klinger's analysis, calculates the formula  $\text{C}^{20}\text{H}^{40}\text{O}^{10}$ .\*

	Calculation.		Analyses.	
	$\text{C}^{20}\text{H}^{40}\text{O}$	$\text{C}^{20}\text{H}^{40}\text{O}^{10}$	De Luca.	Klinger.
Carbon . . . . .	54.5	55.2	54.5	55.2
Hydrogen . . . . .	9.1	7.8	9.1	7.8
Oxygen . . . . .	36.4	37.0	36.4	37.0
	100.0	100.0	100.0	100.0

Cyclamin dissolves readily in alcohol at a gentle heat, and separates again in the amorphous state on cooling or evaporation; it is insoluble in wood-spirit, glycerin, ether, chloroform, sulphide of carbon, volatile oils, and alkalis.

A solution of cyclamin exposed to light in a sealed tube, deposits a white amorphous substance, which redissolves at a moderate heat. Moist cyclamin produces a large crop of cryptogamous plants, among which is a new alga, *Hygrocrocis Cyclamina*.

The aqueous solution of cyclamin absorbs chlorine and bromine, and is coagulated thereby without colour; neither is it coloured by iodine. Hydrochloric acid dissolves it in the cold, and coagulates it at about 80° C. with formation of sugar. Strong sulphuric acid forms with it a yellow liquid, which turns violet after a while, and yields a white precipitate with water. Acetic acid dissolves it in the cold, and does not coagulate it when heated. Nitric acid decomposes it in the cold, and more quickly when heated, forming acid products which have not been examined. Fused with hydrate of potassium, it gives off hydrogen and forms a peculiar sparingly soluble acid. Cyclamin does not reduce an alkaline solution of cupric tartrate. It does not ferment with yeast. Synaptase at 30°–35° C. decomposes it, forming a solution which contains a non-fermentable sugar (De Luca). According to Martius, cyclamin boiled with dilute acids takes up water and is converted into glucose and cyclamiretin, a body not examined:



**CYCLAMIRETIN.** See above.

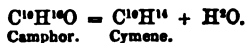
**CYCLOPITE.** A feldspathic mineral, discovered by Waltershausen in the dolerite of a cyclopien rock, near Catania. It forms very small, white, translucent, lozenge-shaped prisms belonging to the trimetric system, the form of which closely resembles that of Anorthite and Labrador. The mean of two analyses gave:—

SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	Ca <sup>2</sup> O	Mg <sup>2</sup> O	Na <sup>2</sup> O	K <sup>2</sup> O	H <sup>2</sup> O
41.45	29.83	2.20	20.83	0.65	2.32	1.71	1.91 = 100.90;

leading to the formula  $3(2\text{M}^{20}\text{O}.\text{SiO}^2) + 2(2\text{Al}^{10}\text{O}^3.3\text{SiO}^2)$  or  $3\text{MO}.\text{SiO}^2 + 2(\text{Al}^{10}\text{O}^3.\text{SiO}^2)$  (Jahresber. d. Chem. 1853, p. 811). If in the first formula ( $\text{M}^{12}\text{Al}^{14}\text{Si}^{20}\text{O}^{30}$ ) we substitute  $\text{al} = \frac{2}{3}\text{Al}$ , it becomes  $3\text{M}^{12}\text{al}^{14}\text{Si}^{20}\text{O}^{30}$  which is reducible to that of an orthosilicate,  $\text{B}^4\text{SiO}^4$ .

**CYMENE** or **CYMOL.**  $\text{C}^{10}\text{H}^{14} = \text{C}^{10}\text{H}^{12}.\text{H}$ . *Cymyl*, *Camphogen*, *Hydride of Cymyl* or *Thymyl*.—A hydrocarbon discovered in 1840 by Gerhardt and Cahours (Ann. Ch. Phys. [3] i. 102, 372; Ann. Ch. Pharm. xxxviii. 101, 345). It occurs, together with hydride of cumyl, in the volatile oil of Roman cumin, obtained from *Cuminum Cuminum* (Gerhardt and Cahours); in the seed of the water-hemlock, *Cicuta virosa* (Trapp, Ann. Ch. Pharm. cviii, 386); in oil of thyme (Lallemand, Ann. Ch. Phys. [3] xlix. 156); and, according to Haines (Chem. Soc. Qu. J. viii. 289), in the volatile oil of *Ptychotis Ajowan*; according to Stenhouse, however, this oil contains, not cymene, but a camphene,  $\text{C}^{10}\text{H}^{14}$ .

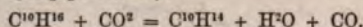
**Formation.**—By the dehydration of common camphor with phosphoric anhydride (Delalande, Ann. Ch. Phys. [3] i. 368) or with chloride of zinc (Gerhardt):



2. By the action of hydrate of potassium on *cymylic alcohol* (Kraut, *Dissertation über Cuminal und Cymen*, Göttingen, 1854).—3. By the action of iodine or nitric acid on *wormseed-oil* (Hirzel, *Zeitschr. Pharm.* 1854, pp. 23, 67; 1855, pp. 84, 181; see

\* In Martius' paper the formula is  $\text{C}^{20}\text{H}^{40}\text{O}^{10}$ , probably a misprint.

also WORMSEED-OIL).—4. By the dry distillation of *coal*, passing over, partly in the lighter, but more abundantly in the heavy oil of coal-tar. The latter yields it by rectification between 170° and 180° C. (Mansfield, Chem. Soc. Qu. J. i. 244).—5. By treating *caoutchou* or oil of turpentine with bromine and sodium alternately (Gr. Williams, Phil. Mag. [4] xxxii. 15).—6. By the action of moist carbonic acid gas at a red heat on oil of turpentine, an oil is produced having the composition of cymene (Deville, Ann. Ch. Phys. [2] lxxv. 66):

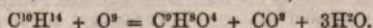


7. Oil of wormwood distilled with phosphoric anhydride and then with potassium yields an oil isomeric, if not identical, with cymene.

*Preparation.*—1. From oil of Roman *cumin*.—When this oil, which is a mixture of cymene and hydride of cumyl (p. 182), is distilled, the cymene passes over first. It cannot, however, be obtained quite pure by simple distillation, as a portion of the hydride of cumyl always passes over with it; the separation may, however, be effected by rectifying the first portions of the distillate with melting potash, which takes up the hydride of cumyl, converting it into cuminate of potassium, and allows the cymene to pass over free (Noad, Phil. Mag. [3] xxxii. 15). A better mode of separation is to shake up the oil with a strong solution of acid sulphite of potassium or sodium, which unites with the hydride of cumyl, forming a crystalline compound and leaves the cymene free (Kraut, Bertagnini). Noad obtained 7 oz. of cymene from 1 lb. of oil of *cumin*.—2. In like manner cymene may be obtained from the oil of *water-hemlock seed*, by separating the hydride of cumyl by means of acid sulphite of sodium, pressing the oily residue, and distilling.—3. From *camphor*, it is obtained by distillation with phosphoric anhydride, or better, with fused chloride of zinc. A few pieces of this substance are placed in a capacious retort, and heated till they melt into a pasty mass. The camphor is then added by small portions, whereupon the mixture swells up and blackens, and a liquid passes over containing a considerable quantity of camphor, from which it may be freed by a fresh distillation over chloride of zinc. This process yields a considerable quantity of cymene with the use of a comparatively small quantity of chloride of zinc.

*Properties.*—Colourless strongly refracting liquid, having a very agreeable odour of lemons; that which is prepared from camphor has a somewhat camphorous odour. Specific gravity = 0.857 at 16° C. (Noad); 0.861 at 14° C. (Gerhardt); 0.8678 at 12° C., and 0.8778 at 0° C. (Kopp). It boils at 171.5° C. (Noad); 175° C. (Gerhardt and Cahours); 177.5° C. (Kopp). Vapour-density 4.59 to 4.70 (Gerhardt and Cahours), by calculation (2 vol.) = 4.64. It is permanent in the air, insoluble in water, but dissolves readily in alcohol, ether, and oils, both fixed and volatile.

*Decompositions.*—1. Cymene is not attacked by strong sulphuric acid in the cold, but fuming sulphuric acid dissolves it, producing cumyl-sulphuric acid,  $\text{SO}^2.\text{C}^{10}\text{H}^{14}.\text{H}$ .—2. Nitric acid of ordinary strength does not attack it in the cold; but on heating the mixture, red vapours are evolved, and the cymene is ultimately converted into toluyllic, and ultimately into nitrotoluyllic acid. With fuming nitric acid the action is very violent, and a yellow resin is formed at the same time (Gerhardt and Cahours). If the nitric acid and the cymene are carefully cooled by immersion in a mixture of ice and salt, and the cold cymene is then added by drops to the nitric acid, nitrocymene,  $\text{C}^{10}\text{H}^{12}(\text{NO}^2)$  is produced (Barlow)\*. A mixture of sulphuric and nitric acid converts it, with aid of heat, into dinitrocymene,  $\text{C}^{10}\text{H}^{12}(\text{NO}^2)^2$  (Kraut, Ann. Ch. Pharm. xxi. 70).—3. Caustic potash has no action on cymene.—4. Chlorine and bromine attack it in the cold, forming chlorinated and brominated compounds which are decomposed by distillation (Gerhardt and Cahours).—5. Chromic acid converts it into insolinic acid,  $\text{C}^8\text{H}^8\text{O}^4$  (Hofmann, Ann. Ch. Pharm. xevii. 197):



#### Derivatives of Cymene.

**NITROCYMENE.**  $\text{C}^{10}\text{H}^{12}\text{NO}^2$ . When cymene cooled by a freezing mixture is cautiously dropped into nitric acid likewise cooled, the mixture first turns brown, then green, and at length acquires the consistence of cream; and by washing it with water, and afterwards with dilute carbonate of sodium, nitrocymene is obtained as a reddish-brown, oily liquid, heavier than water. It is not altered by contact with the air, but when

\* In the preparation of cumylamine by the action of ferrous acetate on nitrocymene (p. 297), Barlow likewise obtained an oil insoluble in hydrochloric acid, and exhibiting, after repeated distillation, the composition and boiling point (175°) of cymene. It differed however from ordinary cymene in this respect, that the nitro-cymene obtained from it by the action of nitric acid floated on water, whereas ordinary nitrocymene is heavier than water. For this reason Barlow distinguishes the cymene and nitrocymene thus obtained as  $\alpha$ -cymene and  $\alpha$ -nitrocymene. Further investigation is however required to establish the distinction.

distilled it yields an oil which floats on water. By the action of ferrous acetate it is converted into cymylamine. (Barlow, Ann. Ch. Pharm. xcvi. 245.)

**DINITROCYMENE.**  $C^{10}H^{14}(NO_2)^2$ . When cymene is added drop by drop to a mixture of 2 pts. strong sulphuric acid and 1 pt. fuming nitric acid heated to about  $50^\circ C$ , and water added after the mixture has been left to itself for an hour or two, a liquid is deposited which solidifies after a while; and on dissolving this product in boiling alcohol, the uncrystallisable portion is deposited on cooling, and dinitrocymene crystallises out on evaporation. It forms rhombic, iridescent tablets, melting at  $54^\circ C$ , soluble in alcohol and ether, insoluble in water. From saturated solutions, it is deposited as an oil. When heated in the air, it decomposes with deflagration, leaving a residue of charcoal. (Kraut, Ann. Ch. Pharm. xcii. 70.)

**CYMENE, BROMIDE OF.**  $C^{10}H^{14}Br^2$  or perhaps  $C^{10}H^{13}Br.HBr$ . When cymene is mixed with water and bromine till the colour of the latter disappears, and the product is washed with soda-solution and with water, bromide of cymene is obtained, as a transparent, colourless, oily liquid, insoluble in water, and but slightly soluble in alcohol. It turns yellow by keeping, giving off hydrobromic acid. It cannot be distilled without decomposition. When boiled with alcoholic potash, it yields a colourless oil, very much like cymene; perhaps  $C^{10}H^{12}$ . (Sieveking, Ann. Ch. Pharm. xcvi. 245.)

**CYMENE, CHLORIDE OF.**  $C^{10}H^{14}Cl^2$  or perhaps  $C^{10}H^{13}Cl.HCl$ . Obtained by passing chlorine gas into water on which cymene floats. It resembles the bromide. Fuming sulphuric acid decomposes it, with evolution of hydrochloric acid, forming a red-brown mass, which when diluted with water forms a solution of cymyl-sulphurous acid. (Sieveking, *loc. cit.*)

When cymene is repeatedly distilled in dry chlorine gas, hydrochloric acid is evolved, and an oil containing 10.7 p. c. chlorine passes over between  $170^\circ$  and  $230^\circ C$ . (Sieveking.)

**CYMENE-SULPHURIC ACID.** Syn. with CYMYL-SULPHUROUS ACID (p. 298).

**CYCID.** Löwig's name for cymyl,  $C^{10}H^{13}$ .

**CYCIDINE.** Syn. with CYMYLAMINE.

**CYMIN.** Syn. with CYMENE.

**CYMINIC ACID.** Syn. with CUMINIC ACID.

**CYMO-GLYCOL.** Syn. with CUMO-GLYCOL.

**CYMOZ.** Syn. with CYMENE.

**CYMOPHANE.** Syn. with CHRYSORREYL (i. 958).

**CYMYL.**  $C^{10}H^{13}$ . The radicle of cymene, cymylic alcohol, &c. The *chloride*  $C^{10}H^{13}Cl$  is produced by passing hydrochloric acid gas into cymylic alcohol (Rossi), perhaps also by the action of chlorine on cymene; the *bromide* also by the action of bromine on cymene. (Sieveking.)

**CYMYLAMINES.** Ammonia-bases containing 1, 2, or 3 at. cymyl in place of hydrogen. Monocymylamine was discovered by Barlow in 1855 (Phil. Mag. [4] x. 454; Ann. Ch. Pharm. xcvi. 245); the other two by Rossi (Compt. rend. li. 570). They are all produced by the action of ammonia on chloride of cymyl; monocymylamine also by the action of reducing agents on nitrocymene.

When a mixture of chloride of cymyl and strong alcoholic ammonia is heated for some hours in a sealed tube placed in the water-bath and then left to cool, sal-ammoniac separates, together with a few drops of oily tricymylamine. The liquid filtered and evaporated leaves a crystalline residue consisting of the hydrochlorates of cymylamine and dicymylamine, mixed with oily tricymylamine, which may be dissolved out by ether, and remains, after evaporation of the ether, as an oil which may be made to crystallise by agitation.—The hydrochlorates of the other two bases are separated by fractional crystallisation from water, the hydrochlorate of dicymylamine being much less soluble in water than the cymylamine-salt. The bases are separated from the hydrochlorates by distillation with potash.

*Cymylamine.*  $C^{10}H^{13}N = N.H^2.C^{10}H^{13}$ .—*Monocymylamine, Cymidine* (Barlow), *Cuminamine primaire* (Rossi). Barlow prepares this base by distilling nitrocymene with iron-filings and acetic acid, the mixture being made up to a stiff paste. A distillate of complex character is then obtained, a considerable portion of which is insoluble in hydrochloric acid. From the portion which dissolves in that acid, soda throws down cymylamine, which, after agitation with ether and evaporation of the ethereal solution, separates as a brown oil, which cannot be distilled without alteration, except in an atmosphere of hydrogen.

Cymylamine is a colourless oily liquid which does not solidify in a mixture of ice



## 298 CYMYLIC ALCOHOL—CYMYL-SULPHUROUS ACID.

and salt (Rossi). It is lighter than water, inodorous, and without action on litmus paper (Barlow). It is volatile at ordinary temperatures, and produces white fumes on the approach of a rod moistened with hydrochloric acid. It begins to boil at about 280° C., with partial decomposition. Boils at about 250° C. (Barlow). It is slightly soluble in water, easily in alcohol and ether.

Cymylamine is violently attacked by nitric acid, and on adding soda to the liquid, a semi-solid substance is separated. Bromine acts but slightly on cymylamine, iodine not at all. Chloride of cyanogen appears to form with cymylamine, a base corresponding to melaniline. Chloride of benzoyl forms, with cymylamine, small crystals probably consisting of benzoyl-cymylamine. Cymylamine absorbs carbonic acid from the air, forming a solid compound. (Rossi.)

Hydrochlorate of Cymylamine,  $C^{10}H^{13}N.HCl$ , is formed by mixing the base with strong hydrochloric acid, as an oily layer, which crystallises on agitation or evaporation (Barlow), in nacreous rhomboidal laminæ (Rossi). It colours deal-shavings yellow, but does not exhibit any particular reaction with hypochlorite of calcium. Its solution colours the skin red. (Barlow.)

Chloroplatinate of Cymylamine,  $C^{10}H^{13}N.HCl.PtCl_2$ , is yellow, sparingly soluble in water, more soluble in alcohol, and still more in ether. The chloro-aurate is yellow, crystalline, sparingly soluble in water.

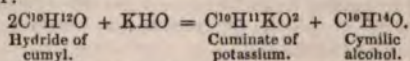
The Sulphate and Oxalate of Cymylamine are white, crystalline, soluble in water. (Barlow.)

Dicymylamine,  $C^{20}H^{27}N = N.H.(C^{10}H^{13})_2$ .—Cuminamine secondaire. Dense, colourless, oily liquid, beginning to boil with decomposition above 300° C. Insoluble in water, soluble in alcohol and ether. The hydrochlorate crystallises in needles slightly soluble in cold water.—The chloroplatinate is sparingly soluble in cold water, and crystallises from alcoholic solution in small roseate needles. (Rossi.)

Tricymylamine,  $C^{30}H^{39}N = N.(C^{10}H^{13})_3$ .—Cuminamine tertiaire. Crystallises in small rhomboidal laminæ, which melt at 81°–82° C. Insoluble in water, very soluble in ether and in boiling alcohol, slightly in cold alcohol. It does not affect the colour of litmus. The hydrochlorate, which crystallises in needles grouped in crosses, is nearly insoluble in water, very soluble in alcohol.—The chloroplatinate crystallises with difficulty; the alcoholic solution deposits it as a viscous mass which solidifies on drying. (Rossi.)

**CYMYL-DITHIONIC ACID.** Syn. with CYMYL-SULPHUROUS ACID.

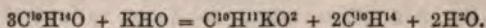
**CYMYLIC ALCOHOL.**  $C^{10}H^{14}O = C^{10}H^{13}.H.O$ . Hydrate of Cymyl. Cuminic Alcohol. (Kraut, *Dissertation über die Derivate des Cuminols und des Cymens*. Göttingen, 1854. Ann. Ch. Pharm. xcii. 66.)—This compound, which is isomeric with hydrate of thymyl (oil of thyme), is produced by the action of alcoholic potash on hydride of cumyl:



When hydride of cumyl is boiled for about an hour with several times its volume of alcoholic potash, in an apparatus which allows the condensed vapours to flow back again, the potash is converted into cuminate, and on adding water to the liquid, an oil separates, consisting of cymylic alcohol and cymene, the latter being produced by a secondary reaction (*vid. inf.*). The oil is agitated with acid sulphite of sodium, to separate any remaining hydride of cumyl, then dried and subjected to fractional distillation.

*Properties.*—Colourless liquid, having a very faint but agreeably aromatic odour, and a sharp spicy taste. It boils at 243° C. without decomposition, and is not acidified by prolonged contact with the air. It is insoluble in water, but soluble in all proportions in alcohol and ether.

*Decompositions.*—1. Heated with potassium, it evolves hydrogen and forms a granular mass, decomposed by water into potash and cymylic alcohol.—2. Heated with nitric acid, it is converted into cuminic acid.—3. Strong sulphuric acid transforms it into a resinous brittle substance which becomes semifluid in boiling water.—4. By boiling with alcoholic potash, it is converted into cuminate of potassium and cymene:



It does not combine with the acid sulphites of the alkali-metals.

**CYMYL-SULPHUROUS ACID.**  $C^{10}H^{14}SO^2 = \frac{(SO)^2}{C^{10}H^{13}.H}O^2$ . Cymene-sulphuric, Cymol-sulphuric, Sulphocymenic, Sulphocymylic, Camphogene-sulphuric, Sulpho-camphic, Thymyl-sulphurous acid. Cymyl-dithionio acid =  $HO.C^{20}H^{18}S^2O^2$  (Kolbe).—

This acid, first obtained by Gerhardt and Cahours (Ann. Ch. Phys. [3] i. 106) from cymene, and almost at the same time by Delalande (*ibid.* i. 368), has been further examined by Sieveking (Ann. Ch. Pharm. cvi. 257). It is produced by the action of fuming sulphuric acid on cymene, and perhaps also on chloride of cymene (p. 297). To prepare it, cymene is dissolved in a slight excess of fuming sulphuric acid, no sulphurous acid being then evolved if the mixture is kept cool; the liquid is diluted with water, saturated with carbonate of lead, and filtered; and the solution of cymylsulphite of lead is evaporated to the crystallising point. The aqueous solution of the crystals decomposed by sulphydric acid and evaporated in vacuo after filtration, yields the acid. As the solution of the lead-salt is apt to decompose during evaporation, and leave a dark brown mass, the solution of which is not decolorised by sulphydric acid, it is better, according to Sieveking, to decompose the barium-salt with sulphuric acid, remove the excess of that acid by carbonate of lead, and the dissolved lead by sulphydric acid.

The acid is obtained, by evaporating its aqueous solution, in small deliquescent crystals. Fuming nitric acid converts it into nitrocymyl-sulphurous acid, the salts of which detonate when heated. (Church, Phil. Mag. [4] ix. 256.)

The cymylsulphites are all soluble in water.

**Cymylsulphite of Barium**,  $C^{10}H^{12}BaSO_3$ , crystallises with 1,  $1\frac{1}{2}$ , and 2 at. water. The hydrated salts have a fine nacreous lustre, and a bitter taste, with nauseously sweet aftertaste. They dissolve easily in water, alcohol, and ether. The aqueous solution may be boiled without decomposition. The water of crystallisation is given off at  $100^\circ C$ . (Gerhardt and Cahours), at  $130^\circ C$ . (Trapp), not completely below  $170^\circ$  (Sieveking).

**Cymylsulphite of Calcium**,  $C^{10}H^{12}CaSO_3 + \frac{3}{2}aq.$ , crystallises in thin colourless laminae, easily soluble in water and alcohol, becoming anhydrous at  $170^\circ C$ . (Sieveking.)

**Cymyl-sulphite of Copper**, obtained by decomposing the barium-salt with sulphate of copper. Crystallises in fine silky needles, or laminae, soluble in water and alcohol. (Sieveking.)

**Cymyl-sulphite of Lead**,  $C^{10}H^{12}PbSO_3 + 2aq.$ —Crystallises in nacreous laminae, which give off all their water at  $120^\circ C$ . (Delalande.)

**Cymyl-sulphite of Silver**.—On dissolving carbonate of silver in the aqueous acid, and evaporating in vacuo, the liquid turns brown and leaves a brown residue containing a few white needle-shaped crystals. (Sieveking.)

**Cymyl-sulphite of Sodium**,  $C^{10}H^{12}NaSO_3 + \frac{3}{2}aq.$ —Obtained by decomposing the barium-salt with sulphate of sodium. Crystallises in fine silky needles or laminae, soluble in water and alcohol, and giving off all their water at  $170^\circ C$ . (Sieveking.)

**CYNAPINE**. A poisonous alkali contained, according to Ficinus (Mag. Pharm. xx. 367), in fool's parsley (*Æthusa Cynapium*). It is said to crystallise in rhombic prisms, to have an alkaline reaction, to be soluble in water and alcohol, and to form a crystallisable sulphate.

**CYNENE**,  $C^{12}H^{18}(?)$ .—A hydrocarbon obtained by distilling wormseed-oil (the volatile oil of *Semen-contra*) several times with phosphoric anhydride, and treating the distillate with strong sulphuric acid to separate a heavy, less volatile oil. Cynene is a mobile colourless oil, permanent in the air, and having a peculiar odour like that of wormseed. It is insoluble in water, very soluble in ether, and boils between  $173^\circ$  and  $175^\circ C$ . Specific gravity 0.825 at  $16^\circ C$ . Gives by analysis 88.8 per cent. carbon and 11.1 hydrogen. It is not attacked by ordinary sulphuric acid, but the fuming acid dissolves it, forming a conjugated acid. Strong nitric acid acts violently upon it when heated, forming a yellow oil heavier than water. (Völckel, Ann. Ch. Pharm. lxxxix. 358.)

**CYNODINE**. An uncrystallisable substance obtained from the root of creeping dog's-tooth grass (*Cynodon dactylon*). (Semmola, *Berzelius Jahresber.* xxiv. 635.)

**CYNOSURUS CRISTATUS**. *Dog's-tail grass*.—This grass, gathered in the flowering season, yields in the fresh state 2.38 per cent., and in the dry state 6.38 per cent. ash, containing in 100 pts. 25.0 per cent.  $K_2O$ , 10.1  $CaO$ , 2.4  $MgO$ , 0.1  $FeO$ , 32  $SO_3$ , 40.1  $SiO_2$ , 7.2  $P_2O_5$ , and 11.6  $KCl$ . (Way and Ogston.)

**CYNURENIC ACID**. Syn. with KYNURENIC ACID.

**CYPERUS ESCULENTUS**. *Earth-almond* (*Erdmandel*).—The tubers of this sedge, which is indigenous in Sicily, Egypt, &c., cultivated in Arabia, and used as food, contain in 100 pts., according to Semmola (J. Chim. méd. xi. 256), 22 pts. starch, 4 inulin, and 1 crystallisable sugar; according to Muñoz y Luna (Ann. Ch. Pharm. lxxviii. 370), 29 starch, 14 cane-sugar, 7 gum and salts, and 28 of a fixed oil resembling oil of sweet almonds. According to Landerer (Buchn. N. Repert, iv. 20), the oil has a specific gravity of 0.94, resembles oil of sesame, and is easily saponifiable.



**CYPRIN.** See VESUVIAN.

**CYPRIPEDIN.** The name applied in North America to a brown powder prepared from *Cypripedium pubescens*, and used as a medicine.

**CYSTINE.** *Cystic oxide*,  $C^2NH^2SO^2$ .—An organic base constituting the chief constituent of a rare kind of urinary calculus, occurring in men and dogs. It was discovered by Wollaston (Phil. Trans. 1810, p. 223), and has been found in renal concretions and urinary gravel (Golding Bird, *Treatise on Urinary Concretions*; Toel, Ann. Ch. Pharm. xvi. 247), in the kidneys of the ox (Cloetta, *ibid.* xcix. 289), and in the liver of a drunkard who died of typhus fever (Scherer, N. Jahrb. Pharm. vii. 306). Researches on cystine and cystic calculi have also been published by Lassaigne (Ann. Ch. Phys. [2] xxiii. 328); Baudrimont and Malaguti (J. Pharm. xxiv. 633); Thaulow (Ann. Ch. Pharm. xxvii. 197); Marchand (J. pr. Chem. xvi. 254); Robert (J. Pharm. vii. 165); Buchner (Repert. xxi. 113); Walchner (Schw. J. xlvii. 106); Wurzer (Schw. J. lvi. 472); Schindler (Mag. Pharm. xxix. 264); Venables (N. Quart. J. of Sc. vii. 30); O. Henry (J. Pharm. xxiii. 11); Dranty (J. Chim. méd. xiii. 230); Taylor (Phil. Mag. [3] xii. 337); Lecanu and Ségallas (J. Pharm. xxiv. 460); Schweig (Heidelb. Medic. Annal. xiii. 364); Bley (Arch. Pharm. [2] ii. 165); Civiale (J. Chim. méd. 1838, p. 355); Schlossberger (N. Jahrb. Pharm. viii. 4).

Urinary calculi are occasionally found consisting of pure cystin, but if the calculus likewise contains phosphate of calcium, the cystine is either dissolved out by ammonia and the filtrate left to evaporate to the crystallising point; or it is dissolved in potash and precipitated from the filtrate by acetic acid. (Lassaigne.)

*Properties.*—In urinary calculi, cystine presents the appearance of a yellowish, shining, confusedly crystallised mass (Wollaston); wax-yellow, translucent, elongated, square octahedrons (Schindler); yellowish, translucent, with a faint lustre; confusedly crystalline; crackles between the teeth; is easily rubbed to a yellowish powder; tasteless, neutral (Robert). Specific gravity of a calculus containing 97.5 pts. cystine to 2.5 pts. phosphate of calcium = 1.577 (Wollaston); of a calculus containing 91 per cent. of cystine = 1.13 (Taylor); of a pure cystine calculus = 1.7143 (Venables). From a solution in hot aqueous potash, cystine slowly crystallises on addition of acetic acid, in neutral six-sided laminae (Wollaston); from an ammoniacal solution by evaporation, in transparent colourless laminae (Lassaigne) in rhombic crystals (Thaulow). (See *Funke's Atlas d. physiolog. Chem.* Taf. v. fig. 6). Cystine is insoluble in water and in alcohol.

*Decompositions.*—1. Cystine yields by dry distillation, carbonate of ammonia, a volatile, viscid, stinking oil, and spongy charcoal (Wollaston and Walchner). It likewise gives off hydrocyanic acid (Schindler).—2. When heated in the air, it gives off a quite peculiar and extremely disagreeable odour (Wollaston), sulphurous and resembling that of oil of mustard (O. Henry). It takes fire at the same time, without melting (Wollaston), assumes a black-brown colour, and splits into fragments, which disappear without fusion or intumescence, emitting a strong smell of hydrocyanic acid and a faint empyreumatic odour (Buchner).—3. Fused with hydrate of potassium, it gives off an inflammable gas, which burns with a flame of sulphide of carbon, producing sulphurous anhydride (Thaulow).—4. Its solution in excess of nitric acid leaves, when concentrated by boiling, first a white opaque substance (Lecanie and Ségallas), then a substance which becomes continually browner, and at last black, is free from oxalic acid (Wollaston), but contains sulphuric acid (Thaulow).

*Combinations.*—Cystine dissolves in the aqueous solutions of the stronger acids; and, on evaporation at a gentle heat, yields crystals which are soluble in water. The solution is precipitated by carbonate of ammonia. The *hydrochlorate, nitrate, phosphate, and sulphate* of cystine crystallise in needles grouped in tufts (Wollaston).

Cystine dissolves readily in aqueous *ammonia, potash, soda, and lime*, also in the *acid carbonates of potassium and sodium*, but not in acid carbonate of ammonia. All these solutions yield granular crystals by evaporation (Wollaston).—From alkaline solutions, cystine is not precipitated by sulphuric, hydrochloric, or nitric acid; but acetic, tartaric, and citric acids precipitate it in a few seconds as a fine white powder. (Wollaston, Lassaigne, Walchner, Robert.)

The solution in ammonia, when left to evaporate, yields pure cystine in crystals.—The solution in potash deposits, on evaporation, white crystalline grains, which are tasteless, leave a small quantity of potash when burned, are insoluble in water, but dissolve readily in water containing potash. (Lassaigne.)

**CYSTINOÏD TUBERCLES.** *Xanthocystin*. A substance resembling cystine and xanthine, and found in small whitish grains on the mucous membrane of the digestive organs, liver, &c. of the body, two months after interment, of a person



who died of inflammation of those organs. (A. Chevallier and Lassaigue, *J. Chim. méd.* [3] vii. 208; *Pharm. Centr.* 1861, p. 717.)

**CYTISINE.** A bitter substance obtained from *Cytisus Laburnum* by Chevallier and Lassaigue (*J. Pharm.* iv. 340; vii. 235). The alcoholic extract of the seeds is treated with water; the solution precipitated with neutral acetate of lead, and the lead removed from the filtrate by sulphydric acid. The liquid filtered from the sulphide of lead leaves, when evaporated, a yellowish green mass of the consistence of an extract, soluble in water and in alcohol, precipitated by basic acetate of lead and nitrate of silver. When taken internally, it produces giddiness, spasms, and vomiting. — According to Peschier (*J. Chim. méd.* vi. 65), cytisine is identical with the cathartine of senna-leaves; but these substances have not been sufficiently studied to decide the question with certainty.

## D.

**DACTYLIS.** The cleansed root-fibres of *Dactylis glomerata*, yield, according to Schulze's analysis (*Ann. Ch. Pharm.* cix. 180), 24 p. c. dry substance containing 9·4 p. c. ash, of which 3·9 pts. (= 41·9 p. c. of the ash) consists of silica.

For Way and Ogston's analysis of the ash of the flower of this plant, see GRASSES.

**DADYL.** The name given by Blanchet and Sell to the camphene obtained from crystallised hydrochlorate of turpentine-oil. (See TURPENTINE, OIL OF.)

**DEDALEA QUERCINA.** This sponge, dried at 100° C., contains 3·2 p. c. nitrogen and leaves 3·1 p. c. ash. (Schlossberger and Döpping.)

**DAGGED.** See BIRCH-TAR (i. 589).

**DAGUERRETYPE.** See LIGHT (CHEMICAL ACTION OF).

**DAHLIA.** The tubers of *Dahlia pinnata* contain 10 p. c. inulin (thence called *Dulcin*), also citric and malic acids, chiefly as calcium-salts, a fixed oil, and a volatile oil which is lighter than water and quickly resinises when exposed to the air. In water this volatile oil solidifies after some time, and yields crystals apparently consisting of benzoic acid. (Payen, *J. Pharm.* ix. 384; x. 239.)

**DALANOVITE.** See DELANOVITE.

**DALARNITE.** Breithaupt's name for the arsenical pyrites from Dalarne or Dalecarlia in Sweden.

**DALLEIOCHIN** or **THALLEIOCHIN.** An imperfectly investigated product of the action of ammonia and chlorine on quinine (*q. v.*).

**DAMALURIC** and **DAMOLIC ACIDS.** Two volatile acids said to exist in cows' and horses' urine. Damaluric acid  $C^6H^{12}O^2(?)$  is oily, heavier than water, and smells somewhat like valerian. (Städeler, *Ann. Ch. Pharm.* lxxvii. 27.)

**DAMASCUS STEEL.** See IRON.

**DAMMARA RESIN, AUSTRALIAN.** *Cowdie gum, Cowdie-pine resin.* The produce of a large coniferous tree, *Dammara Australis*, which grows in New Zealand. It forms white or yellow masses very difficult to break, having a shining fracture, and a very decided odour of turpentine. According to R. D. Thomson (*Ann. Ch. Phys.* [3] ix. 499) it consists of an acid resin, dammaric acid, and a neutral resin, dammaran, the former of which may be extracted by alcohol.

The acid resin is deposited, by spontaneous evaporation of its alkaline solution, in crystalline grains containing 72·64 p. c. carbon, 9·31 hydrogen, and 18·00 oxygen. On precipitating the boiling alcoholic solution with alcoholic nitrate of silver containing ammonia, a precipitate is formed containing 14·60 to 14·75 p. c. oxide of silver. Thomson represents the acid resin by the formula  $C^{76}H^{11}O^7$  (75·4 C and 9·4 H), and the silver-precipitate by  $AgO.C^{76}H^{11}O^7$ .

The neutral resin, insoluble in weak alcohol, yields a colourless varnish with absolute alcohol and with oil of turpentine. Its analysis gives 75·02 C and 9·6 H, which Thomson represents by the formula  $C^{76}H^{11}O^6$ . When exposed to continued heat it absorbs oxygen.

The resin, when distilled alone at a gentle heat, yields an amber-coloured volatile oil called dammarol, containing 82·2 p. c. carbon, and 11·1 hydrogen; and by distilling it with lime, another yellow oil is obtained, called dammarone. All these products require further examination.

**DAMMARA RESIN, EAST INDIAN.** *Dammar-Puti* (i. e. *Cat's-eye resin*, so called on account of its lustre). This is the more ordinary kind of dammara resin; it

## 302 DAMMARIC ACID—DAMMARYL, HEMI-HYDRATE OF.

comes chiefly from Singapore, and is said to be obtained from *Pinus Dammara*, Lamb., or *Dammara alba* (*D. orientalis*, Rumph., or *Agathis loranthifolia*, Salisb.), a coniferous tree, indigenous in the East Indies and in the Moluccas. The resin, which exudes from excrescences on the stem near the root, forms colourless or yellowish, more or less transparent lumps, varying in size between that of a pea and that of a hen's egg; of specific gravity 1.04 to 1.09; having a resinous odour and conchoidal fracture. According to Brandes, it melts at 150° C.; according to Dulk, it begins to melt at 73° C. It dissolves partially in *absolute alcohol* (to about  $\frac{2}{3}$ ) and in *ether* (to about  $\frac{3}{10}$ ); in *aqueous alcohol* it is less soluble in proportion as the alcohol is weaker; *oils*, both *fixed* and *volatile*, dissolve it more completely. It is insoluble in dilute acids, but *strong sulphuric acid* dissolves it completely even in the cold; and on dropping the yellow or red solution into water, a white precipitate is formed, consisting, apparently, of the unaltered resin. The resin heated with sulphuric acid is decomposed, with evolution of sulphurous acid. *Nitric acid* likewise decomposes it with aid of heat. When suspended in water and treated with *chlorine gas*, it takes up 26 p.c. chlorine. It is scarcely attacked by *potash* or *soda*, even when heated therewith; heated with *soda-lime*, it gives off hydrogen and carburetted hydrogen, and if the heat has not been raised above 320° C., a resinous body is found in the residue.

East Indian Dammara resin contains about 0.2 p.c. ash, a small quantity of gum, a hydrocarbon, dammaryl, and three resinous bodies. According to analyses by Schrötter (Pogg. Ann. lix. 37), and Dulk (J. pr. Chem. xlv. 16), the entire resin yields numbers answering to the empirical formula  $C^{80}H^{14}O^5$ .

Weak alcohol extracts from Dammara resin an acid resin called hydrated dammarylic acid (or *a-resin*) amounting to about  $\frac{1}{4}$  of the whole, and consisting of  $C^{80}H^{14}O^7$  (or  $C^{13}H^{27}O^7$ , according to Dulk): it is white, becomes electric by friction, melts at 50° C.; does not oxidise by exposure to the air. It unites with bases, but the salts are very unstable.

If the dammara resin, after exhaustion with weak spirit, be treated with *absolute alcohol*, a resin *b*, consisting of anhydrous dammarylic acid  $C^{13}H^{26}O^3$  (or  $C^{80}H^{14}O^3$ , according to Dulk), is dissolved, and remains, on evaporating the alcohol, as a white powder, melting at 60° C., perfectly soluble in absolute alcohol, in ether, in oils, both fixed and volatile, and in strong sulphuric acid; the alcoholic solution has a stronger acid reaction than that of the resin *a*. With *bases*, it behaves like the resin *a*, forming salts which, according to Dulk, are identical with those of the resin *a*.

When the dammara resin, after exhaustion with alcohol, is treated with *ether*, a portion of the residue (= about  $\frac{1}{4}$  of the original resin) dissolves, and the solution yields by evaporation a hydrocarbon, called dammaryl, =  $C^{80}H^{14}$  (or  $C^{13}H^{26}$  according to Dulk). It is a tasteless, inodorous powder, which becomes electric by friction, dissolves easily in cold ether, softens at 145°, and melts at 190° C. It oxidises quickly when exposed to the air, taking up from 3 to 5 p. c. oxygen (= 1 or 2 at. O, according to the formula  $C^{80}H^{14}O^2$ ). By exposure for some time to moist air at 110° C., it acquires the composition of the crude resin  $C^{80}H^{14}O^5$ . Dammaryl suspended in water and treated with chlorine, yields a substitution-product containing 34 p. c. chlorine.

After the resin has been exhausted with alcohol and ether, there remains an insoluble resin *c*, a hemi-hydrate of dammaryl  $C^{80}H^{14}O$  (or  $C^{80}H^{14}O^2$ , according to Dulk). It is a green, shining, brittle mass, which melts at 215° C., is insoluble in acids and alkalis, but dissolves in oil of turpentine and in the strongest sulphuric acid.

Brandes separated dammara resin into an *a-resin* easily soluble in alcohol and ether, and amounting to about  $\frac{1}{4}$  of the whole, and a  *$\beta$ -resin* or dammarin soluble only in 1000 pts. absolute alcohol and 40 or 50 pts. ether, and insoluble in alkalis.

Dammara resin is much used for the preparation of varnishes (Dingl. polyt. J. cxxviii. 68; cxxxi. 141), for which purpose it is dissolved, after drying, in 2 or 3 pts. of oil of turpentine; to obtain a thicker varnish, it is usual to add a certain quantity of thick turpentine or boiled linseed oil. (Handw. d. Chem. 2<sup>a</sup>. Aufl. ii. [3] 340.)

**DAMMARIC ACID.** The constituent of Australian dammara resin which is insoluble in weak spirit (p. 301).

**DAMMARIN.** See DAMMARA-RESIN, EAST INDIAN.

**DAMMAROL.** }  
**DAMMARONE.** } See DAMMARA-RESIN, AUSTRALIAN.

**DAMMAR-PUTI.** See DAMMARA-RESIN, EAST INDIAN.

**DAMMARYL.** The constituent of East Indian dammara-resin, insoluble in alcohol, soluble in ether.

**DAMMARYL, HEMI-HYDRATE OF.** The constituent of East Indian dammara-resin which is insoluble in alcohol and ether.

**DAMMARYLIC ACID.** The constituent of East Indian dammara-resin, which is insoluble in weak, but soluble in absolute alcohol (p. 302).

**DAMMARYLIC ACID, ANHYDROUS.** The constituent of East Indian dammara-resin, which is soluble in weak alcohol (p. 302).

**DAMOURITE.** A hydrated mica, forming crystalline laminae in the interstices of crystals of kyanite, found at Pontivy in Bretagne. It is colourless, yellowish-white or yellow, transparent in thin laminae, and of scaly texture. Specific gravity 2.792. Hardness = 2.0 to 3.0. Heated in a tube, it gives off water and swells up. Before the blowpipe, it intumesces, becomes white and opaque, and melts to a white enamel. It is decomposed by strong sulphuric acid.

According to Delesse (Ann. Ch. Phys. [3] xv. 248), it consists of  $KO \cdot SiO_2 + 3(Al^{10}O_3 \cdot SiO_2) + 2H_2O$  or  $K_2O \cdot 3Al^{10}O_3 \cdot 6SiO_2 + 2H_2O$ , which (by substituting  $al = \frac{1}{2}Al$ ) may be reduced to  $(Ka^{10}H^2)SiO^{10}$ , the formula of an orthosilicate. It likewise contains a small quantity of fluorine, and appears to be a variety of margarodite.

**DAWATTE.** A mineral consisting of sulphur, arsenic, and iron with a little cobalt, and agreeing in form with arsenical pyrites, of which it is probably only a cobaltiferous variety. Hayes, however (Sill. Am. J. xxiv. 386), assigns to it the formula  $Fe^{10}As^2 \cdot Fe^{10}S^2$ . It is found in the gneiss near Franconia in New Hampshire, United States. (See *Kenngott's Uebers.* 1852, p. 99; *Jahresber. d. Chem.* 1853, p. 778.)

**DANBURITE.** A borosilicate of calcium found at Danbury in Connecticut, in shining, translucent, pale yellow crystals belonging to the trimetric system. Hardness 7 to 7.5. Specific gravity 2.95. Melts before the blowpipe and colours the flame green. Two analyses made by Smith and Brush give the following results:

SiO <sub>2</sub>	Al <sup>10</sup> O <sub>3</sub>	Mn <sup>10</sup> O	Ca <sup>2</sup> O	Mg <sup>2</sup> O	B <sup>2</sup> O <sub>3</sub>	Loss by ignition.	Total.
48.10	0.30	0.56	22.41	0.40	27.73	0.50	100.00
48.20		1.02	22.33		27.95	0.50	100.00

whence Smith and Brush deduce the formula  $3CaO \cdot 2SiO_2 + 3B_2O_3 \cdot 2SiO_2$ , which is equivalent to  $Ca^{10}O \cdot SiO^{10} + B^{10}O^{10} \cdot SiO^{10}$  (Brush, Sill. Am. J. [2] ix. 286. Smith and Brush, *ibid.* xvi. 365. See also *Rammelsberg's Mineralchemie*, p. 770).

**DANNEBORITE.** A variety of hornblende found in the iron mines of Dannemora in Sweden. Its structure is fibrous or radiating, the individual crystals being closely aggregated. Colour yellowish-brown to greenish-brown. Specific gravity 3.516. Blackens before the blowpipe, and in thin pieces melts to a dark slag. Contains:

SiO <sub>2</sub>	Al <sup>10</sup> O <sub>3</sub>	Ca <sup>2</sup> O	Mg <sup>2</sup> O	Mn <sup>2</sup> O	Fe <sup>2</sup> O
48.9	1.5	0.7	2.9	8.5	38.2

corresponding nearly to the formula  $8M^{10}O \cdot 9SiO^{10}$ , where M is almost entirely represented by iron. (Erdmann, *Jahresber. d. Chem.* 1856, p. 846.)

**DAPHNETIN.**  $C^{10}H^{14}O^8$  (Zwenger [1860], Ann. Ch. Pharm. cxv. 8).—A product of the decomposition of daphnin, which when subjected to dry distillation, or heated with aqueous acids, or fermented with emulsin, splits up into daphnetin and glucose:



The same decomposition also takes place under the influence of yeast; but it is necessary first to add glucose to the liquid, in order to set up the fermentation, and even then the decomposition is very imperfect.

**Preparation.**—1. A solution of daphnin in dilute hydrochloric or sulphuric acid is boiled till it turns yellow, then diluted with water and left to cool; the impure daphnetin which separates is dissolved in hot water, and precipitated by neutral acetate of lead; and the yellow precipitate is washed, suspended in hot water, and decomposed by sulphydric acid. The liquid filtered at the boiling heat, deposits daphnetin on cooling.—2. The alcoholic extract of mezereon bark is treated with strong hydrochloric acid, and evaporated on the sand-bath till the acid is completely expelled; the carbonaceous residue is then boiled with water; and the impure daphnetin which separates on cooling is purified as above.—3. The alcoholic extract of mezereon bark yields by dry distillation a distillate containing small needle-shaped crystals of impure daphnetin, which may be purified as above.

**Properties.**—Daphnetin forms small needle-shaped monoclinic prisms having a strong refracting power. It has a slightly astringent taste, and dissolves easily in boiling water, still more in boiling alcohol, sparingly in ether. When heated it emits an agreeable odour, and melts at a temperature above 250° C. to a yellowish mass,



which solidifies in the crystalline form on cooling. In a stream of gas it sublimes easily, even below its melting point; but when heated in a close vessel, it suffers partial decomposition.

Hot *hydrochloric acid* easily dissolves daphnetin without decomposing it; strong *sulphuric acid* dissolves it with decomposition. *Nitric acid* colours it deep red.

*Alkalies* and *alkaline carbonates* dissolve daphnetin, with yellow colour, the solution becoming darker on exposure to the air. *Lime-water* and *baryta-water* form with it yellow precipitates, which also become darker by exposure. *Ferric salts* colour daphnetin green, the colour disappearing, however, on addition of free acid or of excess of ferric salt. *Ferrous salts* produce only a faint greenish colouring in solutions containing excess of daphnetin. Daphnetin reduces an *alkaline cupric* solution, even in the cold; also *nitrate of silver*.

*Lead-compound*,  $C^{10}H^{10}O^{10}Pb^{4}O^{10}$ .—A warm aqueous solution of daphnetin mixed with acetate of lead, yields a light yellow gelatinous precipitate, which when dry forms a brittle mass, dark-coloured in thick layers, translucent with yellow-red colour in thin layers. It dissolves sparingly in water, easily in acetic acid. *Nitric acid* turns it red. On boiling it with water, part of the daphnetin is removed, and a compound richer in lead remains.

**DAPHNIN.**  $C^{10}H^{10}O^{10} + 4H^2O$ .—A crystallisable non-azotised glucoside, occurring in the bark of certain species of *Daphne*. Vauquelin in 1808 (Ann. Chim. lxxxiv. 173), first obtained from *Daphne alpina*, an acrid volatile substance soluble in water, to which Berzelius gave the name of daphnin.—C. G. Gmelin and Baer (Schw. J. xxxv. 1) afterwards prepared the body now called daphnin, which has since been more particularly examined by Zwenger (Ann. Ch. Pharm. cxv. 1). It occurs in the bark of the common mezereon plant (*Daphne mezereum*), and somewhat more abundantly in that of *D. alpina*.

*Preparation*.—1. The alcoholic extract of the bark of *D. mezereum* or *D. alpina* is exhausted with water; the solution is precipitated with acetate of lead; the precipitate washed with water, and decomposed by sulphydric acid; and the filtrate evaporated to dryness and treated with absolute alcohol. Daphnin then crystallises from the alcoholic solution (Gmelin and Baer).—2. The alcoholic extract of fresh mezereon bark stripped off in the early flowering time, is dissolved in water; the solution is first precipitated with neutral acetate of lead; the filtrate is subsequently mixed with excess of basic acetate of lead and boiled for a long time; and the resulting precipitate is washed and decomposed by sulphydric acid. The filtrate yields crystallised daphnin on evaporation or on addition of alcohol. (Zwenger.)

As daphnin is soluble in ether, it may be advantageously prepared from the residual bark left after the preparation of *Extr. mezerei athereum*.

*Properties*.—Daphnin crystallises in colourless, transparent, rectangular prisms, sparingly soluble in cold, more freely in warm water, more soluble still in alcohol, especially at the boiling heat, insoluble in ether. The aqueous solution concentrated by heat, tastes bitter at first, afterwards astringent. According to Gmelin, it is neutral when pure, but according to Zwenger, the saturated aqueous solution is decidedly acid.

The crystals of daphnin give off their water at  $100^{\circ}$  C. At a stronger heat daphnin emits an agreeable odour, like that of coumarin. When cautiously heated in small quantities, it melts at about  $200^{\circ}$  C. to a colourless mass, which solidifies again in the crystalline form on cooling; but the melting point and decomposing point are so close together, that unless the heat is very carefully applied, vapours are given off, the residue continues amorphous after cooling, and then forms a yellow precipitate with neutral acetate of lead, and a green mixture with sesquichloride of iron, showing that it contains daphnetin (p. 303). Daphnin heated in a close vessel is decomposed, yielding a sublimate of daphnetin and a residue of charcoal; when heated in the air, it burns with a bright flame. *Nitric acid* decomposes it in the cold and colours it red, and when boiled converts it partly into acetic acid.

*Alkalies* and *alkaline carbonates* dissolve daphnin in the cold, forming a yellow solution which quickly turns brown-red on exposure to the air, especially if warmed. The yellow solution of daphnin in *baryta-* or *lime-water* yields a gelatinous precipitate when heated. Neutral *ferric chloride* imparts a bluish colour to the aqueous solution of daphnin; the liquid turns yellowish when boiled, and deposits a deep yellow precipitate on cooling. *Basic acetate of lead* colours the solution of daphnin yellowish in the cold, and on boiling the liquid an insoluble compound is deposited. *Hydrated oxide of lead* also precipitates daphnin on continued boiling. *Nitrate of silver* forms no precipitate in the cold, but a slight reduction takes place on boiling, and a considerable reduction on addition of ammonia. It reduces an *alkaline cupric* solution only after prolonged boiling.—By heating with aqueous acids, or by the action of emulsion or of yeast, daphnin is resolved into daphnetin and glucose (p. 303).

**DAPICHO** or *Zaspis*. The South American name of the dirty-white spongy caoutchouc which exudes from the roots of *Siphonia elastica*. It is blackened over an open fire, and used for making stoppers.

**DARWINITE**. The name applied by Forbes (Phil. Mag. [4] **xx**. 423) to a mineral from Chili, identical with the Whitneyite (*q. v.*) of Genth.

**DASSIPIIS**. See **HYTRACUM**.

**DATES**. *Dactyli*. The fruit of the date-palm (*Phoenix dactylifera*). They are generally gathered in the ripe state and exposed to the sun, whereby they lose their original bitterness and acquire a pure sweet taste. The fleshy portion of the fruit contains, according to Bonastre (J. Pharm. xviii. 784), crystallisable sugar; according to Reinsch (Buchn. Repert. lxxi. 36) only fruit-sugar (58 p.c.), together with pectin (9 p.c.), gum, and other substances. Kletzinsky (Jahresber. d. Chem. 1858, p. 434) found that dates contain 85 p.c. fleshy substance, 10 kernel, and 5 husk; and the dates freed from the kernel contain in 100 pts.: 36 sugar, 9 pectin and pectinous matter, 23 pts. of other substances soluble in water, 30 water, 0.1 coumarin, citric acid, and other substances. The kernels contain, according to Reinsch, 36 pts. gummy substance and 40 cellulose, together with tannin, fat, &c.

The juice of the flower-buds of the date-palm, which is very rich in sugar, is used for the preparation of arrack, and on the small scale for the preparation of crystallisable sugar. According to Fourcroy and Vauquelin, the pollen of the flowers contains a large quantity of free malic acid.

**DATHOLITE**. *Datolite*. *Dystomite*. *Humboldite*. *Botryolite*. *Esmarkite* (in part). *Natrocalcite* (in part). *Borate of Lime*. *Borosilicate of Lime*. *Chaux boratée silicieuse*. A borosilicate of calcium, crystallising, according to Kopp, in monoclinic combinations, with numerous faces, the primary form of which is the monoclinic prism  $\infty P$  of  $77^{\circ} 30'$  with a nearly rectangular base, deviating only  $10'$  from perpendicularity. The combinations exhibit also the prism  $\infty P 2 = 116^{\circ} 9'$ ; the transverse hemidome  $2P\infty = 43^{\circ} 56'$ , the hemipyramid  $P = 122^{\circ} 0'$ , and many others. Cleavage indistinct parallel to  $\infty P$  and the transverse faces. On the other hand, Brooke and Miller, and Dana (Mineralogy, ii. 335) regard the crystals as trimetric and hemihedral, with cleavage parallel to  $\infty P\infty$  and  $\infty P\infty$ . The crystals are small and glossy, having the form of short prisms or thick tablets, often implanted. The mineral also occurs massive, with coarse or fine-grained structure.

Hardness = 5.0 to 5.5. Specific gravity = 2.9 to 3.1. Colour white, or with a shade of green, yellow, grey, or red. Streak white. Lustre glassy on the crystalline, waxy on the fractured surfaces. Translucent. Fracture uneven, subconchoidal. Brittle.

Ignited in a tube, it gives off water. Before the blowpipe, it swells up and melts easily to a clear glass, occasionally with a greenish or a reddish tint. Colours the flame green. Dissolves in borax; in phosphorus-salt it leaves a skeleton of silica, and if added in considerable quantity forms an enamel-white glass. With a small quantity of soda it forms a clear glass; with a larger quantity, the bead becomes opaque on cooling, and with a still larger quantity, the mass sinks into the charcoal. With gypsum, it fuses to a clear bead.

Analyses: *a.* Andreasberg in the Harz (Stromeyer, Pogg. Ann. xii. 157).—*b.* Andreasberg (Du Menil, Schw. J. lii. 364).—*c.* Andreasberg (Rammelsberg, Pogg. Ann. xlvii. 175).—*d.* Arendal in Norway (Rammelsberg, loc. cit.).—*e.* Isle Royal, Lake Superior (Whitney, Sill. Am. J. [2] xv. 435).—*f.* Nieder-Kirchen, Rhenish Bavaria (Dellmann, Rammelsberg's Mineralchemie, p. 507).—*g.* From the gabbro of Tuscany (Bechi, Sill. Am. J. [2] xiv. 65).

	SiO <sup>2</sup>	B <sup>2</sup> O <sup>3</sup>	CaO	H <sup>2</sup> O	
<i>a.</i>	37.36	21.26	35.67	5.71	= 100
<i>b.</i>	38.51	21.34	35.59	4.67	= 100.04
<i>c.</i>	38.48	20.31	35.64	5.57	= 100
<i>d.</i>	37.65	21.24	35.41	5.70	= 100
<i>e.</i>	37.64	21.88	34.68	5.80	Mn <sup>2</sup> O <sup>3</sup> trace = 100
<i>f.</i>	37.44	24.63	32.23	5.70	= 100
<i>g.</i>	37.50	22.63	35.34	1.56	MgO 2.12 Al <sup>2</sup> O <sup>3</sup> 0.85 = 100

These analyses of the purer specimens lead to the formula  $\text{Ca}^2\text{O} \cdot 2\text{SiO}^2 + \text{Ca}^2\text{O} \cdot \text{B}^2\text{O}^3 + \text{aq.} = \text{Ca}^2\text{Si}^2\text{O}^4 \cdot 2\text{CaB}^2\text{O}^3 + \text{aq.}$ , or  $2\text{Ca}^2\text{O} \cdot \text{SiO}^2 + \text{B}^2\text{O}^3 \cdot \text{SiO}^2 + \text{aq.} = 2\text{Ca}^2\text{SiO}^4 \cdot \text{B}^2\text{SiO}^4 + \text{aq.}$  (calc. 38.15 SiO<sup>2</sup>, 21.15 B<sup>2</sup>O<sup>3</sup>, 34.67 CaO, 5.58 H<sup>2</sup>O). According to Fownes and Sullivan (Pogg. Ann. Ergänz. ii. 368), datholite contains a small quantity of phosphoric acid.

Datholite occurs in numerous localities, among which, in addition to the above, may

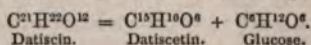


be mentioned Toggiana in Modena, the island of Utoë near Sweden, the Seisser Alp in the Tyrol, and Bergen Hill in New Jersey. It is found in amygdaloid and gneiss; sometimes also in beds of iron ore in primitive rocks.

*Botryolite*, a variety of datholite occurring in botryoidal concretions, is usually regarded as containing twice the quantity of water shown by the above formula (i. 651). An analysis by Rammelsberg gave 36.085 per cent  $\text{SiO}_2$ , 12.340  $\text{B}^2\text{O}_3$ , 35.215  $\text{CaO}$  and 8.686 water; but Dana is of opinion that additional analyses are required to show that this amount of water is constant.

**DATISCA CANNABINA.** *Bastard Hemp.* This plant, indigenous in the Levant and in India, is much used in India, Italy, the south of France, and other places for communicating a permanent yellow dye to silk. According to Braconnot, the leaves contain a peculiar colouring matter, datisca-yellow, which is prepared by precipitating the aqueous decoction of the leaves with a small quantity of neutral acetate of lead, filtering to separate the gummy precipitate thereby formed, mixing the filtrate with potash, then precipitating completely with acetate of lead, decomposing the yellow precipitate with sulphuric acid, and evaporating the filtrate. Datisca-yellow then remains in the form of a pale yellow-brown, translucent mass, insoluble in cold alcohol, but easily soluble in water. The solution is coloured lighter by acids, darker by alkalis and by ferrous sulphate, bright yellow by alum. Stuffs mordanted with alum are dyed permanently yellow by it. Walzl recommends a concentrated decoction of the plant mixed with a little potash as a yellow ink (Handw. d. Chem. 2<sup>te</sup> Aufl. ii. [3] 377).

**DATISCETIN**,  $\text{C}^{15}\text{H}^{10}\text{O}^6$  (Stenhouse [1856], Ann. Ch. Pharm. xviii. 166). A product of the decomposition of datiscin, obtained by treating the latter body with aqueous acids, or with strong potash, not by the action of yeast or emulsin:



When datiscin is boiled with dilute sulphuric acid, the liquid becomes turbid in a few minutes, and deposits datiscetin in colourless needles.

As datiscetin crystallises very easily, it may also be prepared from the mother-liquor obtained in the preparation of datiscin, by precipitating this liquor with basic acetate of lead, decomposing the washed precipitate with sulphydric acid, evaporating the filtrate, and boiling it with dilute sulphuric acid. The datiscetin thus obtained is easily purified by recrystallisation.

Datiscetin is tasteless, nearly insoluble in water, easily soluble in alcohol, and is precipitated therefrom by water. It dissolves in all proportions in ether, and crystallises in needles on evaporation.

Datiscetin melts at a somewhat high temperature, and, if carefully heated, may be partially sublimed. When strongly heated, it takes fire and burns away.

Nitric acid acts violently on datiscetin, even in the cold, nitrous acid being evolved and a resinous substance formed, which ultimately dissolves with red colour; on evaporating the liquid, picric acid is obtained, but no oxalic acid. Boiled with weak nitric acid (1 pt. ordinary nitric acid to 10 pts. water), it yields nitrosalicylic acid. Distilled with sulphuric acid and acid chromate of potassium, it yields oily drops, which smell like salicylic acid, and colour ferric salts purple. When datiscetin is gradually added to melting hydrate of potassium, it dissolves with deep orange colour and evolution of hydrogen; and on supersaturating the cooled mass with hydrochloric acid, a resinous substance separates, which, when heated, yields a colourless sublimate of needle-shaped crystals, having the aspect of benzoic acid, but giving with ferric chloride the reaction of salicylic acid.

Datiscetin dissolves in aqueous alkalis, and is reprecipitated by acids. An alcoholic solution of datiscetin forms with neutral acetate of lead a deep yellow precipitate, consisting of  $\text{C}^{15}\text{H}^8\text{Pb}^2\text{O}^6$ .

**DATISCIN.**  $\text{C}^{21}\text{H}^{22}\text{O}^{12}$ . A glucoside closely allied to salicin. It was first obtained by Braconnot in 1816 (Ann. Ch. Phys. [2] iii. 277), from the leaves of *Datisca cannabina*, and to a great extent correctly examined; but his statements were so far forgotten, that the body was universally regarded as identical with inulin, till Stenhouse in 1855 (Ann. Ch. Pharm. xviii. 166; Chem. Gaz. 1856, No. 318) re-examined the roots of *Datisca cannabina*, and showed that the body obtained by Braconnot was really a distinct compound.

*Preparation.*—The alcoholic extract of the root is evaporated to a syrup and mixed with half its bulk of water; the liquid is decanted from a resin which separates; and the impure datiscin which crystallises by spontaneous evaporation is pressed between paper, and then dissolved in alcohol; on subsequent addition of water, a further portion of resin separates, and the dilute solution after a while yields purer datiscin. By repeat-



ing the treatment with alcohol and water it is obtained quite pure. It may also be freed from tannin by mixing the alcoholic solution with a small quantity of gelatin, the purification being completed as above.

**Properties.**—Pure datiscin forms colourless silky needles. It is sparingly soluble in cold, somewhat more easily in hot water, easily in cold alcohol, and in all proportions in boiling alcohol, very slightly in ether. From a strong alcoholic solution it is immediately precipitated by water, from a weaker solution after some time only; from the ethereal solution it separates by spontaneous evaporation in large crystalline laminae. The solutions of datiscin have a very bitter taste, and a neutral reaction.

Datiscin melts at  $180^{\circ}\text{C}$ .; on carefully heating it in a current of air, it yields a small quantity of a crystalline sublimate. When more strongly heated alone, it is carbonised, and gives off the odour of burnt sugar. When boiled with dilute sulphuric or hydrochloric acid, it is easily resolved into crystallisable sugar and datiscetin (p. 306.) Yeast and emulsin do not appear to act upon it. Dilute nitric acid dissolves it even in the cold, converting it into picric and oxalic acids. Stronger nitric acid forms the same products.

Datiscin, although neutral to test-paper, nevertheless exhibits with bases the properties of a weak acid, dissolving with deep yellow colour in aqueous alkalis, and in lime- and baryta-water, and being separated therefrom by acids. The aqueous solution of datiscin forms a light yellow precipitate with acetate of lead, either neutral or basic, also with stannic chloride, greenish with cupric salts, brownish with ferric salts. By boiling with strong potash-ley, it is decomposed, with formation of datiscetin. Melting potash acts in like manner, but the resulting datiscetin suffers further decomposition (p. 306).

#### **DATOLITE.** Syn. with DATHOLITE.

**DATURA.** A genus of plants belonging to the solanaceous order. The herb and seed, especially the latter, of the common thorn-apple, *Datura Stramonium*, contain a poisonous alkaloid, daturine, which, according to Plants, is identical with atropine. The herb and seeds contain also an organic acid, which Peschier (N. Trommsd. xxv. 2, 83) regarded as peculiar, and distinguished by the name daturic acid; but according to Brandes (Buchn. Repert. viii. 1), it is nothing but malic acid. The ash of the seed contains 17.8 per cent. potash, 12.6 soda, 3.6 lime, 16.5 magnesia, 3.4 ferric oxide, 30.6 phosphoric anhydride, 4.6 silica, and 10.2 charcoal. (Souchay, J. pr. Chem. xxxviii. 32.)

The flowers of thorn-apple are said also to exert a poisonous action. The leaves and seeds are used medicinally as a narcotic.

The seeds of *Datura arborca* contain daturine, malic acid, fixed oil, &c. The ash contains in 100 pts. 8.5 potash, 4.5 soda, 7.0 lime, 11.4 magnesia, 9.5 alumina, 21.2 silica, 5.7 sulphuric anhydride, 2.5 chlorine, and 13.4 carbonic anhydride. (Walz, J. pr. Pharm. xxiv. 355.)

**DAUCUS CAROTA.** The carrot. The roots of this well known esculent contain a red colouring matter, carotin,  $\text{C}^{18}\text{H}^{20}\text{O}$ , together with a colourless substance hydrocarotin,  $\text{C}^{18}\text{H}^{20}\text{O}$ , from which the red compound is probably formed by oxidation as the root ripens. (See CAROTIN, i. 806.)

Carrots contain, according to Wackenroder, a colourless volatile oil, sugar, and starch, and the residue left on evaporating the recently expressed juice, contains 9.3 per cent. uncrystallisable sugar, 0.3 carotin, 1.0 fixed oil, together with starch, malic acid, albuminous substances, ash, &c.

Bibra found in fresh carrots 87.4 per cent. water, and in the air-dried root 15.1 per cent. water, 0.05 fat and carotin, 0.6 resin and oil, 29.0 sugar, 3.0 inulin, 2.8 albumin, 11.8 organic acid, and 37.8 cellulose. Schmidt found in carrots grown on various soils, from 86.5 to 87.0 water, and in the dry substance 7.2 to 8.0 cane-sugar. Völkel found in 100 pts. of fresh carrots, 87.3 per cent. water, 6.5 sugar, 0.2 oil, 0.8 gum and pectin, 0.6 nitrogen-compounds, and 3.4 cellular tissue.

Ritthausen found in large field-carrots weighing from 168 to 1255 grms., from 84.5 to 87.8 per cent. water, and in the dry substance 1.0 to 1.3 per cent. nitrogen, and 6.0 to 8.7 per cent. ash-constituents. The proportion of nitrogen in the entire carrot is 0.3 per cent. (Boussingault), 0.2 (Millon), 0.2 to 0.3 (Schmidt). (Handw. d. Chem. 2<sup>te</sup> Aufl. ii. [3] 381.)

For Way and Ogston's analysis of the ash of the carrot, see vol. i. p. 807.

#### **DAUPHINITE.** Syn. with ANATASE.

**DAVIDSONITE.** An impure variety of beryl, found in the coarse-grained granite vein near Tory in Aberdeenshire, and in the Rubieslaw mine. Contains 12.5 per cent. glucina.

**DAVY LAMP.** The miner's safety-lamp. (See vol. i. p. 1101.)

**DAVYNE.** A variety of nepheline from Vesuvius. See NEPHELINE.

**DAVYTE.** Syn. with STYPTERITE.

**DECANTATION.** The separation of a clear liquid from a precipitate or deposit by inclining the vessel and suffering the liquid to run out. The best form of vessel for the purpose is the ordinary beaker glass having its edge inclined outwards, but not turned over, and rendered smooth by fusion, not cut or ground. The sides should be perpendicular or slightly inclining outwards from top to bottom, and the bottom flat, or with only a slight indentation inwards in the middle. It is important that the sides and bottom be of uniform thickness, so that the beaker may be heated in the sand-bath without fear of cracking, as the application of heat is often necessary to make a precipitate subside completely.

The glass should not be filled above  $\frac{2}{3}$  or  $\frac{3}{4}$  of its depth, as otherwise the stream of liquid which runs out on inclining the vessel, makes too sharp an angle with the side, and a portion of it is very apt to run down the edge. In many cases this inconvenience may be obviated by smearing the edge with a little tallow or lard; but with hot liquids, or such as dissolve fats, like caustic alkalis or ether, this method is of course inapplicable. The decantation may often be greatly facilitated by holding a wet glass rod in a nearly vertical position against the edge of the beaker, so as to cause the stream of liquid to run down it: this method prevents the liquid from running down the sides of the beaker, and also enables it to run into the lower vessel without splashing.

It is only, however, from very heavy precipitates that a liquid can be thus decanted without carrying some of the solid particles with it. For preparations, in which the loss of a few particles is unimportant, simple decantation is often advantageously resorted to; but for quantitative analysis, excepting when the precipitates are very heavy, like metallic gold, or clotted, like chloride of silver, complete separation cannot be effected without filtration. This operation and the subsequent washing may, however, be greatly facilitated by first leaving the precipitate to subside as completely as possible, then pouring the clear liquid as above into the filter, and after it has run through, rinsing the precipitate in the beaker with pure water, pouring this through the filter, again washing the precipitate with water, and so on, till the greater part of the soluble matter is removed. The precipitate is then to be poured on to the filter, and the washing completed. This mode of proceeding saves time, and enables the washing to be performed with a much smaller quantity of water than if the liquid and precipitate were at once thrown in the filter. (For further details, see Handw. d. Chem. 2<sup>te</sup> Aufl. i. 11, art. ANGIENEN.)

**DECHENITE.** A native vanadate of lead from the Lauter valley near Niederschlettenbach in Rhenish Bavaria, where it occurs in botryoidal crystalline masses and scaly deposits, of dark red to yellowish colour, translucent, with waxy lustre on the recently fractured surfaces. Specific gravity = 5.81. Hardness = 4.0. Melts easily before the blowpipe to a yellowish bead; on charcoal it yields globules and a deposit of lead, sometimes emitting an odour of arsenic. With borax and phosphorus-salt, it gives the reactions of vanadium; with soda it melts to a white enamel. Soluble in dilute nitric acid and in hydrochloric acid.

According to C. Bergmann's analysis, the dark red variety contains 47.2 per cent.  $V_2O_5$  and 52.9  $Pb_2O$ ; the yellowish variety, 49.27  $V_2O_5$  and 50.57  $Pb_2O$ ; whence the formula  $Pb_2O.V_2O_5$  or  $PbVO_3$ . According to Brush (Sill. Am. J. [2] xxiv. 116), it contains a considerable quantity of zinc, and is identical with aræoxene (i. 354).

**DECOCTION.** The operation of boiling. This term is likewise used to denote the liquid itself, which has been made to take up certain soluble principles by boiling.

**DECREPITATION.** The crackling noise which several salts make when suddenly heated, accompanied by a violent exfoliation of their particles. The effect is generally due to the sudden conversion of the water enclosed within their substance into steam; not, however, the combined water, for the salts which decrepitate most powerfully are anhydrous salts, chlorate of potassium and nitrate of lead, for example; and those which contain water of crystallisation generally fuse quietly when heated. The water, which is the cause of decrepitation, is merely mechanically enclosed between the solid particles of the body. Decrepitation, especially in natural minerals, is also frequently due to the unequal expansion of the laminae which compose them, in consequence of their being imperfect conductors of heat, like glass and cast iron. The true cleavage of minerals may often be detected in this way, for they fly asunder at their natural fissures.

**DECOLORIMETER.** An instrument invented by Payen for estimating the decolorising power of charcoal. It depends upon the fact that a longer column of a comparatively lighter coloured liquid exhibits by transmitted light the same depth of colour as a proportionally shorter column of a more strongly-coloured solution.

(Diction. Techn. viii. 532. Dingl. Polyt. J. xxvii. 372; Handw. d. Chem. 2<sup>te</sup> Aufl. ii. [3] 383.)

**DECOMPOSITION.** See CHEMICAL AFFINITY (i. 853).

**DEGEROÏTE** or **DEGERÖHITE**. An amorphous brown mineral, found near Stansvik, on Degerö, not far from Helsingfors in Finland. It contains, according to Thoreld's analysis, 36.6 p. c. silica, 13.7 water, 41.4 ferric oxide, 1.16 ferrous oxide, 2.9 lime, 2.5 magnesia, 0.8 alumina, and a small quantity of phosphoric acid: it appears to be a product of decomposition. (Arppe, *Analyser af finska mineralier*, p. 18.)

**DEIAMBRA**, or *Congo Tobacco*, is a plant growing wild in the marshy districts of Congo, the flowers of which produce a narcotic effect when smoked, and are much used in the locality.

**DELANOVITE**. A manganiferous bole from Michac, Dep. de Dordogne, in France. It is amorphous, reddish-white or red, slightly translucent on the edges. Hardness = 1 to 1.5. Fracture splintery. Lustre slightly waxy. Adheres strongly to the tongue, and becomes somewhat plastic by immersion in water. Decomposed by sulphuric acid. An analysis by C. v. Hauer gave 50.55 SiO<sub>2</sub>, 19.15 Al<sub>2</sub>O<sub>3</sub>, 0.63 CaO, 4.40 Mn<sub>2</sub>O, 24.05 H<sub>2</sub>O (total 98.78). Of the water, 14.05 pts. go off at 100° C., and the remainder at a red heat. (Jahresber. d. Chem. 1853, p. 829.)

**DELESSITE**. Ferruginous chlorite. (See CHLORITE, i. 914.)

**DELIQUESCENCE**. The property which certain very soluble salts and other bodies possessed of absorbing moisture from the atmosphere, and dissolving therein.

**DELPHIN**. *Delphinin*, *Phocenin*, *Dolphin-fat*, *Huile de Dauphin*. (Chevreul [1818] Ann. Ch. Phys. [2] xxii. 374.—*Recherches sur les corps gras*. pp. 190, 287, and 467.—Berthelot, Ann. Ch. Phys. [3] xli. 251.)

A neutral fat found in the oil of *Delphinus globiceps*, *D. Phocæa*, and *D. marginatus*; it has not yet been obtained in the pure state, the olein not having been completely separated.

To prepare it, 100 pts. of dolphin-oil are dissolved in 90 pts. of warm alcohol of specific gravity 0.797; the solution is decanted from the oil which precipitates on cooling, and distilled with water; the oil which remains in the retort, and consists of a mixture of delphinin and olein, is separated from the watery liquid and treated with cold dilute alcohol; and the alcohol is evaporated, after the solution has been separated from the undissolved olein.

Delphin is an oil very mobile at 17° C.; specific gravity 0.954 (Chevreul), 0.948 (Berthelot). It has a faint, peculiar, somewhat ethereal odour, like that of valeric acid. Does not redden litmus. Boiling point 258° C. (Berthelot.)

It dissolves abundantly in hot alcohol. The alcoholic solution, diluted with a large quantity of water, and distilled, leaves delphin, which reddens litmus from containing free valeric acid. The fat, when exposed to warm air, likewise acquires the power of reddening litmus, and a powerful odour proceeding from the liberated valeric acid. Delphin heated to 100° C. with an equal quantity of oil of vitriol, and then left to itself, gives off, after a week, the odour of valeric and sulphurous acids; water added to it takes up sulphuric, sulphoglyceric, and valeric acid, and glycerin, and leaves an oily mixture of valeric acid, oleic acid, and a small quantity of unsaponified fat. 100 pts. delphin saponified with potash, yield 36 pts. valeric acid, 59 pts. oleic acid, and 15 pts. of glycerin.

100 pts. of the oil of the common porpoise (*Delphinus Phocæa*) saponified with baryta yielded 82.2 pts. of fixed fatty acids, 16.0 pts. phocenate (valerate) of barium, and 14.0 glycerin, or 6.7 pts. glycerin to 10.0 pts. valeric acid (C<sup>10</sup>H<sup>16</sup>O<sup>4</sup>). The same oil treated with alcohol yielded successively three oils, containing respectively 4.4 pts., 4.4 pts. and 5.1 pts. glycerin to 10. pts. valeric acid. The first of these three oils when again treated with alcohol, yielded a new liquid (phocenin) containing 2.7 pts. glycerin to 10 pts. of valeric acid (Chevreul). The oil of *Delphinus globiceps* was found to contain, besides fixed fatty acids and ethal, 5.9 pts. glycerin to 10.0 valeric acid. Now for 10 pts. of valeric acid, monovalerin contains 9.0 pts.; divalerin 4.5 pts., and trivalerin 3.0 pts. of glycerin. Hence it appears that phocenin is intermediate in composition between the artificial valerins, and may therefore be regarded as a mixture of them—a conclusion further warranted by its separation into valeric acid and glycerin by saponification. (Berthelot.)

**DELPHINIC ACID**. *Phocenic acid*. The acid thus denominated by Chevreul, and discovered by him, first in dolphin-oil and afterwards in the ripe berries of the guelder rose, is now known to be identical with valeric acid.



**DELPHININE.** (Lassaigne and Feneuille (1820), Ann. Ch. Phys. xii. 358. Brandes, Schw. J. xxv. 369. O. Henry, J. Pharm. xviii. 661. Couerbe, Ann. Ch. Phys. lii. 352.) An alkaloid discovered by Lassaigne and Feneuille, in the *Delphinium Staphisagria*, or *Stavesacre*. It is thus obtained:—

The seeds, deprived of their husks, and ground, are boiled in a small quantity of distilled water, and then pressed in a cloth. The decoction is filtered, and boiled for a few minutes with pure magnesia. It must then be refiltered, and the residue left on the filter well washed, and then boiled with highly rectified alcohol, which dissolves out the alkali. By evaporation, a white pulverulent substance, presenting a few crystalline points, is obtained.

It may also be procured by the action of dilute sulphuric acid on the bruised but unshelled seeds. The solution of sulphate thus formed is precipitated by carbonate of potassium. Alcohol separates the base from this precipitate in an impure state. It may be purified by treating it with boiling water to separate a small quantity of nitre, then digesting the residue with ether, which dissolves out the pure delphinine, and evaporating the ethereal solution (Couerbe). The matter insoluble in ether Couerbe designates as *Staphisaine*.

Delphinine is slightly yellow, but yields a nearly white powder. It does not crystallise. Its taste is bitter and acrid. When heated it melts, and on cooling becomes hard and brittle like resin. If more highly heated, it blackens and is decomposed. Water dissolves a very small portion of it. Alcohol and ether dissolve it very readily. The alcoholic solution renders syrup of violets green, and restores the blue tint of litmus reddened by an acid. It forms soluble neutral salts with acids. Alkalis precipitate the delphinine in a white gelatinous state, like alumina.

Sulphate of Delphinine does not crystallise, but becomes a transparent mass like gum. It dissolves in alcohol and water, and its solution has a bitter acid taste.

Nitrate of Delphinine, when evaporated to dryness, is a yellow crystalline mass. If treated with excess of nitric acid, it becomes converted into a yellow matter, little soluble in water, but soluble in boiling alcohol. This solution is bitter, is not precipitated by potash, ammonia, or lime-water, and does not appear to contain nitric acid, though it is not alkaline. It is not destroyed by further quantities of nitric acid, nor does it form oxalic acid. Delphinine is distinguished from strychnine and morphine by not assuming a red colour when treated with nitric acid. The hydrochlorate is very soluble in water.

The Acetate of Delphinine does not crystallise, but forms a hard transparent mass, bitter and acrid, and readily decomposed by cold sulphuric acid. The oxalate forms small white plates, resembling in taste the preceding salts. (Lassaigne and Feneuille.)

Delphinine produces nausea when taken internally, and excites a prickly burning sensation when rubbed on the skin. It is said to act on the nervous system, and is used as a remedy in chronic swellings of the glands.

**DELPHINITE.** Syn. with **EPIDOTE**.

**DELPHINIUM.** The seeds of *Delphinium Staphisagria* contain, in 100 pts., 19.1 pt. of an oil for the most part soluble in alcohol, 1.4 stearin, 8.1 delphinine, together with gum, starch, &c. According to Couerbe, they contain also staphisagrine, and according to Hofschläger, a peculiar acid.

**DELPHINONE.** Syn. with **VALERONE**.

**DELVAUKITE.** *Delvauxene*. A hydrated ferric phosphate occurring at Berneau near Visé in Belgium, in black or brown-black kidney-shaped masses, having a perfectly conchoidal fracture. Before the blowpipe, it melts to a green magnetic globule. Its composition may be expressed, according to Rammelsberg, by the formula  $2\text{Fe}^{\text{e}}\text{O}^{\text{s}}.\text{P}^{\text{s}}\text{O}^{\text{s}} + 24\text{H}^{\text{s}}\text{O}$ , but it is generally mixed with carbonate of calcium and silica. C. v. Hauer (J. pr. Chem. lxiii. 15) analysed two specimens of this mineral: *a*. from the locality above mentioned, *b*. from Leoben in Styria. The former gave off 12.2 p. c. water at 100° C., and 13.84 p. c., more at a red heat; the latter 12.8 p. c. at 100°, and 13.91 at a red heat. After drying over chloride of calcium, the former contained 17.02 p. c. water, the latter 16.79. These last amounts of water are adopted in the calculation of the following analyses, after deducting 2.08 silica in *a* and 1.24 silica in *b*:

	$\text{P}^{\text{s}}\text{O}^{\text{s}}$	$\text{Fe}^{\text{e}}\text{O}^{\text{s}}$	$\text{Ca}^{\text{s}}\text{O}$	$\text{H}^{\text{s}}\text{O}$	Total.
<i>a</i> .	20.93	52.03	7.94	19.08	99.98
<i>b</i> .	20.04	52.54	8.37	19.04	99.99

From these analyses, Hauer deduces the formula  $2\text{Ca}^{\text{s}}\text{O}.\text{P}^{\text{s}}\text{O}^{\text{s}} + 5\text{Fe}^{\text{e}}\text{O}^{\text{s}}.\text{P}^{\text{s}}\text{O}^{\text{s}} + 16\text{H}^{\text{s}}\text{O}$ .

**DEMIDOFFITE.** A mineral from Nischne Tagilsk in the Ural, where it occurs as a thin coating on malachite; it was formerly called blue malachite. Its surface

is tolerably specular, and covered with fine cracks. Colour sky-blue, sometimes with a tinge of green. It is amorphous, translucent on the edges; brittle. Hardness = 2. Specific gravity 2.25. It consists essentially of cupric silicate. Analysis gave 31.55 SiO<sub>2</sub>, 9.53 Al<sub>2</sub>O<sub>3</sub>, 33.14 Cu<sub>2</sub>O, 3.15 Mg<sub>2</sub>O, and 23.03 H<sub>2</sub>O. (Nordenskiöld, Sill. Am. J. xxiv. 116.)

**DENDRACHATES.** Moss agate (i. 62).

**DENDRITES.** Dendritic or arborescent forms indicate imperfect crystallisation, the crystals laying themselves end to end in long aggregations, somewhat like the branches of a tree. This mode of grouping is particularly frequent in bodies which crystallise in the regular system; striking examples are afforded by the native metals, copper, silver, and gold. The ores of manganese also frequently form dendrites in cracks of rocks, and even in the interior of minerals, as in compact magnesite, and in the variety of carbonate of calcium used as lithographic stone. Good examples of artificial dendrites are afforded by the so-called lead and silver trees, formed by precipitating those metals from their solutions by another metal. Remarkable dendritic crystallisations of iodide and chloride of potassium are described by Warington (Chem. Soc. Qu. J. v. 136; viii. 31; see also CRYSTALLOGRAPHY, p. 159).

**DEOXIDATION.** The abstraction of oxygen. This term is to a certain extent synonymous with reduction, but it is sometimes restricted to partial abstraction of oxygen, the term reduction being applied to the total abstraction of that element: thus peroxide of manganese is said to be deoxidised by heat; oxide of silver to be reduced; this distinction is, however, not very frequently made. The abstraction of oxygen (or other electro-negative radicle) from a compound is evidently equivalent to the addition of a metal (or other positive radicle); thus the conversion of ferric oxide Fe<sub>2</sub>O<sub>3</sub> into ferrous oxide FeO, is the same as the addition of Fe to the former, whereby it is converted into Fe<sub>3</sub>O<sub>4</sub>. A deoxidising agent may therefore be called a metal-adding agent.

**DEPHLEGMATION.** An old term, applied to the process of freeing spirituous or acid liquids from water (*phlegma*). The apparatus used for this purpose in distilleries are called dephlegmators.

**DEPHLOGISTICATION**, or the abstraction of phlogiston, was, according to Stahl's theory, the process of combustion (i. 1089). The "dephlogisticated" bodies of this system were in part the same as those now called "oxidised:" thus oxygen was dephlogisticated air, litharge was dephlogisticated lead, chlorine was dephlogisticated muriatic acid, &c.

**DEPILATORIES.** Substances used for removing the hair. Such are rhusma (*Rhusma turcorum*), sulphurate of calcium, &c.

**DERMATITE.** *Dermatite*.—A silicate of iron and magnesium, M<sup>2</sup>SiO<sub>3</sub> + 2aq.; occurring at Waldheim in Saxony, in kidney-shaped and stalactitic masses, unctuous to the touch, of dark green or brownish colour. Hardness = 2.5. Specific gravity 2.1. Decrepitates and blackens before the blowpipe.

According to two analyses by Fiecinus (Min. Ges. zu Dresden, ii. 216) it contains:

SiO <sub>2</sub>	Mg <sub>2</sub> O	Fe <sub>2</sub> O	Mn <sub>2</sub> O	H <sub>2</sub> O	CO <sub>2</sub>	AlO <sub>3</sub>	Ca <sub>2</sub> O	Na <sub>2</sub> O
35.80	23.70	11.33	2.25	25.20	0.42	0.83	0.83	0.50 = 100.03
40.17	19.33	14.00	1.17	22.00	0.83	0.83	1.33	SO <sub>2</sub> = 0.43 = 100.10

**DENSITY.** See SPECIFIC GRAVITY.

**DESCLOIZITE**, PbVO<sub>3</sub> or 2PbO.VO<sub>3</sub>. An ore of vanadium from La Plata. It is found in rhombic crystals 1 or 2 millimetres thick, of a dark olive colour and strong lustre, reddish-brown by transmitted light, and yielding a brown streak. Hardness 3.5. Specific gravity 5.839. The crystals are united in botryoidal groups and are implanted on quartz-rock, together with pyromorphite. On charcoal before the blowpipe, the mineral yields a metallic bead of lead, together with a black slag. Dissolves in cold dilute nitric acid, leaving a residue of manganic oxide and quartz. The mean of two analyses gave 22.46 per cent. V<sub>2</sub>O<sub>5</sub>, 54.70 PbO, 2.04 ZnO; 0.90 Cu<sub>2</sub>O, 5.32 Mn<sub>2</sub>O, 1.50 Fe<sub>2</sub>O<sub>3</sub>, 2.20 H<sub>2</sub>O, 0.32 Cl and 9.44 insoluble residue, consisting of manganic oxide and silica. (A. Damour, Ann. Ch. Phys. [3] xli. 72.)

**DESCMID.** See STILBITE.

**DESOXALIC ACID.** Syn. with RACEMO-CARBONIC ACID.

**DETONATION.** The noise accompanying the sudden decomposition of a compound or mixture of chemical compounds, or the sudden combination of two or more substances, as the union of oxygen and hydrogen under the influence of heat or



electricity, of chlorine and hydrogen under that of light, the decomposition of fulminating silver, of chloride or iodide of nitrogen, &c., the combustion of sulphur or phosphorus when mixed with chlorate of potassium, and struck or triturated, the explosion of gunpowder, &c. In all these cases, the noise is due to the concussion of the air resulting from the sudden production of a large quantity of gas; a mixture of oxygen and hydrogen exploded by the electric spark in a tightly closed vessel, produces no report.

**DEUTO-COMPOUNDS.** The proper use of the prefix *deuto* (from *deuteros*) is to denote the second in order of the terms of any series: thus, in the several series of oxides  $\text{Fe}^2\text{O}$ ,  $\text{Fe}^3\text{O}^2$ ;  $\text{Mn}^2\text{O}$ ,  $\text{Mn}^3\text{O}^2$ ,  $\text{Mn}^4\text{O}^3$ ;  $\text{Pb}^2\text{O}$ ,  $\text{Pb}^3\text{O}^2$ ,  $\text{Pb}^4\text{O}^3$ ;  $\text{SnO}$ ,  $\text{SnO}^2$  the compounds  $\text{Fe}^3\text{O}^2$ ,  $\text{Mn}^4\text{O}^3$ ,  $\text{Pb}^4\text{O}^3$ ,  $\text{SnO}^2$  are, properly speaking, the deutoxides of the respective metals, the *deuto* denoting simply the place of the compound in the series, not its atomic composition. Such, indeed, was the original use of this prefix; but it has often been confounded with *bi* or *di*, which properly refers to the constitution of the compound, as compared with that of the *proto*- or *mono*-compound of the same series. It is not at present so much used as formerly.

**DEVONITE.** Syn. with WAVELLITE.

**DEWEYLITE.** An amorphous hydrated silicate of magnesium, occurring with serpentine at Middlefield, Massachusetts, in Texas county, Pennsylvania, at Bare Hills, Maryland, and in the Tyrol. Hardness = 2 to 3.5. Specific gravity = 2.246, Middlefield (Shepard); 2.19 to 2.31, Bare Hills (Tyson); 2.216 *ibid.* (Thompson); 1.936 to 2.155 Tyrol (Vellacher). Colour, whitish, yellowish, wine-yellow, greenish, reddish. Translucent. Brittle and often much cracked. Before the blow-pipe it decrepitates, becomes opaque, and fuses with great difficulty on the edges. In powder it borax with a transparent glass.

*Analyses.*—*a.* Middlefield (Shepard, Sill. Am. J. xviii. 31, 1830; analysis imperfect).—*b.* Texas, Pennsylvania (Brush, *Dana's Mineralogy*, ii. 286).—*c.* Bare Hills (Thompson, Phil. Mag. 1843, 191).—*d.* Tyrol (Vellacher, Zeitsch. Geol. Gesellsch. iii. 222).—*e.* *Ibid.* (Kobell, Münch. gel. Ang. xxxiii. 1).—*f.* *Ibid.* (Widtermann, Jahrb. geol. Reichsanst. iv. 525.)

	$\text{SiO}_2$	$\text{Mg}^2\text{O}$	$\text{Ca}^2\text{O}$	$\text{H}_2\text{O}$	$\text{Al}^3\text{O}^3$	$\text{Fe}^3\text{O}^3$	
<i>a.</i>	40	40	..	20	..	..	= 100
<i>b.</i>	43.15	35.95	..	20.25	trace	..	= 99.35
<i>c.</i>	40.16	36.00	0.80	21.60	trace	1.16	= 99.72
<i>d.</i>	40.40	35.85	..	22.60	..	0.38 Apatite	0.78 = 100
<i>e.</i>	41.50	38.30	..	20.50	..	..	= 100.30
<i>f.</i>	40.82	36.06	..	21.72	..	0.42, $\text{CO}^2$	0.59 = 99.61

Hence the formula  $4\text{Mg}^2\text{O} \cdot 3\text{SiO}_2 + 6 \text{ aq.}$  or  $2\text{Mg}^2\text{SiO}^3 \cdot \text{Mg}^4\text{SiO}^4 + 6 \text{ aq.}$

The mineral from Bare Hills, and that from the Tyrol, analysed by Widtermann, have been called *gymnite*; but they belong to the same species as the rest.

An earthy variety from the Tyrol yielded 49.06  $\text{SiO}_2$ , 28.50  $\text{Mg}^2\text{O}$ , 16.25  $\text{H}_2\text{O}$ , 0.69  $\text{Fe}^3\text{O}^3$ , 4.76  $\text{CO}^2$  (= 99.28). (Widtermann.)

**DEXTRIN.**  $\text{C}^6\text{H}^{10}\text{O}^5$ , or  $\text{C}^6\text{H}^{10}\text{O}^{10}$ . *British gum. Leicocome.* (Biot and Persoz, Ann. Ch. Phys. [2] lii. 72. Payen, *ibid.* lv. 225; lxi. 372; lxx. 225, 334. Guérin-Varry, *ibid.* lx. 68. Jacquelin, *ibid.* [3] viii. 225. Béchamp, Compt. rend. li. 256. Gm. xv. 185.)—When starch is subjected to a high temperature, or to the action of dilute acids or alkalis, or of diastase, it is converted into a new substance, identical in composition, but possessing totally different properties, being completely soluble in boiling water, and forming a solution which turns the plane of polarisation of a luminous ray to the right; hence the name *dextrin*. This compound is also formed from starch by the action of saliva, bile, blood-serum, pancreatic juice and other animal matters, and by the action of light upon starch-paste.

*Preparation.*—1. By submitting starch to gentle *torrefaction*. The starch in the state of powder is placed in a thin layer in a shallow iron vessel with double bottom containing oil, which is heated to a temperature not exceeding  $160^\circ \text{C}$ ; it may also be heated in revolving cylinders, like those used for roasting coffee. The operation is finished when the substance exhibits a light brown colour, and exhales the odour of strongly baked bread.

2. One part of starch is acted upon by  $\frac{1}{4}$  pt. oil of vitriol and 2.8 pts. water. The acid is mixed with part of the water, and the starch stirred up with the rest; the diluted acid is gradually poured upon the starch, and the mixture is kept for some time at  $90^\circ \text{C}$ . The dextrin is precipitated by alcohol from the clarified solution (Biot and Persoz). Dextrin so prepared cannot be purified from sugar which is formed at the same time and adheres to it, except by dissolving it at least ten times in water, and precipitating the solution with alcohol, which should not be employed in excess.



3. By the action of *dilute acids* aided by heat. To convert 1000 pts. of dry starch into dextrin by this process, it is mixed with 2 pts. of nitric acid of 36° Bm. diluted with 300 pts. of water, and spread in layers about an inch thick on brass drawers placed in an oven heated to 110° or 120° C. The transformation into dextrin is completed in about an hour and a half. (Payen.)

4. By the action of *diastase*. 400 pts. of water are heated to about 75° C. with 5 pts. of ground malt, and 500 pts. of starch added by small portions at a time. The starch dissolves, and, as soon as the solution is complete, the water is rapidly heated to the boiling point, to arrest the action of the diastase and prevent the formation of glucose. The solution is then filtered and concentrated to the consistence of syrup, in a boiler heated by steam and provided with a mechanical agitator. The second process yields the purest product.

*Properties.*—Dextrin is an uncrystallisable, solid, translucent substance having the aspect of gum arabic. It is soluble in *water* and in *dilute alcohol*, but insoluble in absolute alcohol. The aqueous solution is perfectly limpid and becomes gummy by concentration. Its optical rotatory power is 138·68° to the right (Payen) = 176° (Béchamp.)

*Decompositions.*—1. Dextrin is not coloured blue by *iodine*.—2. By boiling with *dilute acids* and with *caustic alkalis*, it is converted into glucose. When a solution of dextrin is mixed with a small quantity of *caustic potash*, and a dilute solution of *sulphate of copper* added drop by drop, the liquid acquires a deep blue colour and remains limpid in the cold; but if heated above 85° C. it quickly decomposes and deposits a red crystalline precipitate of cuprous oxide. This property distinguishes dextrin from gum arabic.—3. Dextrin heated with *nitric acid* does not yield mucic acid, but only oxalic, and perhaps a little saccharic acid.—4. A mixture of *nitric* and *sulphuric acids* converts dextrin into a nitro-compound resembling xyloidin, soluble in water, precipitable by sulphuric acid (Flores Domonte and Ménard, Compt. rend. xxiv. 391). According to Béchamp, this compound is dinitro-dextrin,  $C^4H^4(NO^2)_2O^3$ .—5. A solution of *baryta* in wood-spirit forms with dextrin a copious precipitate insoluble in wood-spirit, but soluble in excess of water, especially when hot; it contains 46·7 per cent. baryta (Payen).—6. Dextrin is also precipitated by *lime*.—7. The solution of dextrin in water or in aqueous alcohol does not precipitate either neutral or basic *acetate of lead*; but on adding ammonia, a white precipitate is formed containing  $C^4H^4O^3 \cdot Pb^2O$ . When heated to 180° C. it turns yellow and appears to lose  $\frac{1}{2}$  at. water (Payen). Dextrin is precipitated by *stannous chloride*, but not by *ferrous sulphate*.

*Uses.*—Dextrin is applied to a variety of useful purposes; it may, indeed, be used in almost all cases in place of gum arabic. It is employed for stiffening calicos and other cotton stuffs, for the application of mordants in calico printing, for the sizing of paper, for the adhesive layer at the back of postage-stamps, &c. In surgery it is used for making bandages, which become very hard when dry, but are easily removed by means of warm water.

For these technical uses, the crude solution of dextrin is often used, just as it is obtained by the action of diastase or sulphuric acid upon starch; in the latter case, the free acid is neutralised with chalk and the liquid evaporated. The syrup of dextrin thus produced likewise contains unaltered starch, sugar and water, the relative quantities of these substances varying according to the mode of preparation. Dextrin-syrup is very liable to decomposition.

*Estimation.*—To estimate the quantity of dextrin in a solution likewise containing glucose, Gentile determines the total amount of both these bodies by means of a standard solution of potassio-cupric tartrate, and then estimates the glucose with an alkaline solution of ferricyanide of potassium (red prussiate), which does not act upon dextrin. The difference of the two determinations gives the quantity of dextrin.

In the viscous fermentation of saccharine liquids, a gummy matter is formed which bears considerable resemblance to dextrin. It is soluble in water, uncrystallizable, insoluble in alcohol, and precipitated by alcohol from its aqueous solution. Dried at the heat of the water-bath, it is vitreous, transparent, and exactly resembles gum-arabic, with which it likewise agrees in composition; nitric acid converts it into oxalic acid (Tilloy and MacLagan, Phil. Mag. [3] xxviii. 12).

Béchamp has lately shown (Compt. rend. xlii. 1210) that the production of dextrin by the action of dilute acids or of diastase on starch is preceded by the formation of an intermediate substance, which may be called *soluble starch*, inasmuch as it is soluble in water, but retains the power of forming a blue colour with iodine. This soluble starch possesses an optical rotatory power much greater than that of dextrin. [See STARCH.]

*Cellulose dextrin.*—Cellulose subjected to the action of strong sulphuric acid yields a product resembling ordinary dextrin in many of its properties, but deflecting the

plane of polarization  $85^{\circ} 9'$  to the left instead of to the right, and yielding a somewhat different product with nitric acid. (Béchamp.)

**DEXTRIN-SUGAR.** This name is applied by Ventzke to an uncrystallisable dextro-rotatory sugar, probably a mixture of dextrin and glucose.

**DEXTRIN SYRUP.** See DEXTRIN.

**DEXTRO-RACEMIC** or **DEKTROTARTARIC ACID.** Ordinary tartaric acid is thus designated, to distinguish it from *laevo-racemic*, *laevo-tartaric*, or *anti-tartaric acid* (see i. 348; also TARTARIC ACID and RACEMIC ACID).

**DIABASE.** This name, synonymous partly with *greenstone*, partly with *diorite*, is applied to rocks consisting of crystallo-granular mixtures of augite with felspar (oligoclase or labradorite) usually interpenetrated with earthy or scaly chlorite. Diabase has a specific gravity of 2.80 to 2.95; it is massive, coarse or fine-grained, often strongly fissured, sometimes with columnar or laminar separations, sometimes having a slaty structure. The oligoclase and labradorite in the mixture form either distinct crystals, or tabular or granular crystalline aggregates, of a white, greyish, or greenish-white colour, also reddish or brownish. The augite is granular, or in prisms of various lengths, green, brown, or black, often resembling hypersthene. The chlorite, which penetrates the entire mass and gives it a green tint, is probably not an original constituent of the rock, but a product of decomposition, inasmuch as the amount of the water found by analysis is too great to be ascribed wholly to chlorite. (Handw. d. Chem. 2<sup>te</sup> Aufl. ii. [3] 420.)

**DIABETIC SUGAR.** The sugar found in considerable quantity in the urine in cases of *Diabetes mellitus*, was formerly regarded as a distinct kind of sugar, but is now known to be identical with dextro-glucose. (See GLUCOSE, SUGAR, and URINE.)

**DIACLASITE.** A variety of augite, intermediate in composition between diallage and hypersthene, found in the Harzburg forest in the Harz. According to Köhler's analysis (Pogg. Ann. xiii. 101), it contains 53.7 per cent. silica, 25.1 magnesia, 11.5 ferrous oxide, 3.7 water, 1.3 alumina, and 0.2 manganous oxide. Hausmann (*Handb. d. Mineral.* ii. 498) regards it as a distinct species; but the large amount of water, and the comparatively low degree of hardness of the mineral (= 3.5 to 4.0) indicate an advanced stage of decomposition.

**DIADOCHITE.** *Phosphoreisensinter.*—A mineral consisting of hydrated ferric phosphate and sulphate, from the alum-slate near Gräfenhain and Saalfeld in Thuringia. It occurs in reniform or stalactitic masses, with curved lamellar structure and conchoidal fracture. Hardness = 3. Specific gravity = 2.03. It is translucent or opaque, with waxy lustre, and wax-yellow to yellowish-brown colour. Streak white. Heated in a tube it gives off a large quantity of acid water. Before the blowpipe it swells up and fuses on the edges to a black magnetic scoria. According to Plattner's analysis (*Rammelsberg's Mineralchemie*, p. 360) it contains 14.82 per cent.  $P_2O_5$ , 15.4  $SO_3$ , 39.69  $Fe_2O_3$ , and 30.35 water, agreeing nearly with the formula,  $3Fe_2O_3 \cdot 2P_2O_5 + 2(Fe_2O_3 \cdot 2SO_3) + 32H_2O = 4(SO_3)^{10} \cdot O^{23} + 32H_2O$ . When heated with water it gives up 12.6 per cent.  $SO_3$ , but no ferric oxide.

**DIAGOMETER.** An electrical apparatus, intended for the detection of adulterations in olive oil, this oil being said to have less electric conducting power than other fixed oils. (Rousseau, *J. Pharm.* ix. Dec. 1833.)

**DIAGONITE.** Syn. with BREWSTERITE.

**DIAGRYDIUM.** An obsolete name of scammony.

**DIALLAGES.** *Schiller-spar* (in part).—A variety of augite, occurring chiefly in *gabbro*, a rock closely related to serpentine. It is thin-foliated and easily cleavable; laminae brittle. Colour, various shades of green, grey, and brown, sometimes bronze, or nearly metallic. Specific gravity 3.11 to 3.227. It is related to bronzite and hypersthene, but is distinguished from them by the large amount of lime which it contains. A specimen from Odern, analysed by Delesse (*Ann. Min.* [4] xvi. 34) gave 49.30 per cent.  $SiO_2$ , 17.61  $Mg_2O$ , 15.43  $CaO$ , 9.43  $FeO$ , 0.51  $Mn_2O$ , 5.50  $Al_2O_3$ , 0.30  $Cr_2O_3$ , 0.85 loss by ignition.

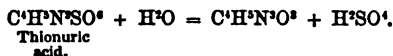
(For other analyses, see *Rammelsberg's Mineralchemie*, p. 465.) Diallage heated in a tube yields water, and assumes a paler colour; on charcoal it fuses with difficulty on the edges to a grey slag; with borax it forms a glass coloured by iron. Bischof (*Chemical and Physical Geology*, ii. 331) regards diallage, bronzite, and hypersthene as altered augites, and supposes that a further alteration might convert them into serpentine.

**DIALLAGITE DIALLOGITE DIALOGITE.** Native carbonate of manganese (i. 789).

**DIALTYL-UREA.** See CARBAMIDE (i. 754) and SINAPOLINE.

**DIALURAMIDE.** *Uramil*.  $C^4H^3N^2O^3 = N.C^4H^3N^2O^3.H^2$ . (Liebig and Wöhler, Ann. Ch. Pharm. xxvi. 274, 313 and 323.)—Laurent, regarding dialuric acid as dibasic, derives dialuramide from 2 at. ammonia, and writes it  $C^4H^3N^2O^3 = N^2.C^4H^3N^2O^3.H^4$ .

This compound is formed when solutions of alloxantin and chloride of ammonium, both freed from air by boiling, are mixed together; it crystallises out, and the mother-liquor contains alloxan and hydrochloric acid (see ALLOXANTIN, i. 139). It is also prepared by boiling an aqueous solution of thionuric acid, or thionurate of ammonium, with dilute hydrochloric or sulphuric acid, till it becomes turbid, and allowing it to cool; even if the solution be not concentrated, it solidifies to a crystalline magma of dialuramide:

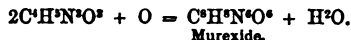


Dialuramide forms white hard needles, united in tufts, having a silky lustre, and turning red when exposed to air containing a trace of ammonia. It is insoluble in cold water; slightly soluble in boiling water, whence it separates on cooling. Soluble in cold sulphuric acid, and precipitated unchanged by water; soluble in cold potash or ammonia, and reprecipitated by acids.

*Decompositions.*—1. Dialuramide treated with *nitric acid* evolves nitrous fumes, and forms a solution which yields alloxan on evaporation, nitrate of ammonium remaining in solution:



2. When a hot dilute solution of *potash* is saturated with dialuramide, ammonia is evolved, and a pale-yellow solution formed, which absorbs oxygen from the air, gradually becomes purple, and deposits gold-yellow crystals of potassic purpurate. The mother-liquor contains alloxanate and mesoxalate of potassium.—3. A solution of dialuramide in *ammonia* is decomposed by boiling, turns purple, and on cooling deposits crystals of ammonic purpurate (murexide). The same solution mixed with aqueous alloxan yields murexide. Murexide is also obtained when argentic or mercuric oxide is gradually added to dialuramide suspended in boiling water, the metal being reduced, without evolution of gas, and a purple liquid formed; the slightest excess of oxide decolorises the solution, which then contains ammonic alloxanate:

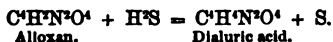


4. When a solution of dialuramide in *sulphuric acid* is diluted till it begins to be turbid, and boiled for some time, the water being renewed, uramilic acid separates on cooling, ammonic sulphate being simultaneously formed. If too much sulphuric acid be present, no uramilic acid is obtained.—5. Dialuramide heated with aqueous *cyanate of potassium*, is converted into pseudo-uric acid. (Schlieper and Baeyer, Pogg. Ann. cxii. 79.)

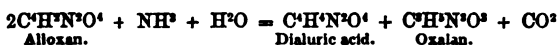


F. T. C.

**DIALURIC ACID.**  $C^4H^3N^2O^4$ . (Liebig and Wöhler, [1838] Ann. Ch. Pharm. xxvi. 276.)—This acid is the final product of the action of reducing agents on alloxan. It is formed: 1. When sulphuretted hydrogen is passed through a boiling aqueous solution of alloxan until no further action takes place:



2. Together with other products, by the action of cyanide of ammonium or cyanide of potassium on aqueous alloxan:

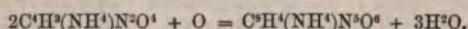




The hydrocyanic acid does not itself enter into these reactions, but merely acts in the manner of a ferment. (Streckker, Ann. Ch. Pharm. cxiii. 49.)

Dialuric acid is prepared by dissolving dialurate of ammonium in warm hydrochloric acid; dialuric acid crystallises out on cooling. Dialurate of ammonium is thus prepared:—1. By saturating with sulphuretted hydrogen a boiling aqueous solution of alloxan, filtering from deposited sulphur, and neutralising the acid filtrate with carbonate of ammonium.—2. By treating aqueous alloxan with zinc and hydrochloric acid, decanting from the precipitated alloxantin, and adding to the solution sufficient carbonate of ammonium to redissolve the precipitated hydrate of zinc.—3. By adding hydrosulphate of ammonium to a solution of uric acid in dilute nitric acid, until the mixture is barely acid to litmus; washing the resulting precipitate with cold water, dissolving it in boiling water, and neutralising the solution with carbonate of ammonium, when it solidifies into a crystalline mass of dialurate.

Dialuric acid forms colourless needles, resembling those of alloxantin; they must be rapidly separated from the mother-liquid and dried. They redden litmus strongly; they are not very soluble in water. The acid neutralises alkalis completely, forming definite salts, dialurates, which are sparingly soluble in cold water, and in the dry state are permanent in the air. The ammonium-salt crystallises in silky needles, which become rose-coloured when dried at the ordinary temperature, and blood-red at 100° C., being converted into purpurate of ammonium:

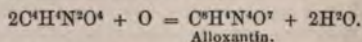


Their solution reduces silver-salts. The barium-salt is white.

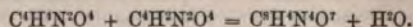
According to the above formula, dialuric acid is monobasic; Laurent regards it as dibasic, and proposes to double its formula.

*Decompositions.*—1. An aqueous solution of dialuric acid is decomposed by boiling, oxalic acid and other products being formed.

2. Dialuric acid (crystallised, or in aqueous solution) is converted into alloxantin by exposure to the air (see ALLOXANTIN, i. 138):



3. Aqueous dialuric acid mixed with aqueous alloxan deposits crystals of alloxantin:



F. T. C.

**DIALYSIS.** A term applied by Graham to the separation of certain substances by liquid diffusion. Soluble substances exhibit great diversity in their degrees of diffusive mobility, and may be divided, as regards this property, into two classes, the more diffusible being either themselves crystallisable, such as common salt and sugar, or closely related to the crystalline class, such as alcohol: hence they are called crystalloids; while the less diffusible are those which are incapable of crystallising, but exhibit a great tendency to assume the gelatinous form; these are called colloids, after gelatin (*colle*), which may be regarded as the type of the class: among these may be mentioned hydrated silicic acid, hydrated alumina and other sesquioxides of the aluminous class when in the soluble state, also starch, dextrin, gum, caramel, tannin, albumin, gelatin, and extractive matters both animal and vegetable. The diffusion of these bodies is extremely slow.

Now it is found that certain gelatinous substances, such as starch-paste, animal mucus, pectin, Payen's vegetable gelose, and other colloidal hydrates, are easily permeable, when in mass, to the more highly diffusible class of bodies, but offer great resistance to the passage of the less diffusive, and are completely impervious to colloidal substances like themselves. Hence such substances afford an easy means of separating crystalloidal from colloidal bodies, when the two exist together in a liquid: a mere film of the jelly is sufficient to produce the separation. A very convenient substance for the purpose is the vegetable or paper-parchment, obtained by immersing unsized paper for a short time in sulphuric acid of a certain strength (i. 819). A sheet of this parchment stretched on a hoop of thin wood, or gutta percha, forms a very convenient dialyser. The fluid to be dialysed is poured into the hoop to the depth of about half an inch, and the whole is floated on water. The more diffusive substances then pass through the septum, leaving the less diffusive behind.

When a mixture of sugar and gum was placed in the dialyser,  $\frac{3}{4}$  of the sugar passed through the membrane in 24 hours without a trace of the gum. When a solution of silicate of sodium mixed with hydrochloric acid was treated in like manner,  $\frac{2}{3}$  of the silicic acid was left upon the dialyser at the end of five days, without a trace of hydro-

chloric acid or chloride of sodium. Half a litre of urine dialysed for 24 hours gave up all its crystalloidal constituents to the water, without a trace of mucous or gelatinous matter, so that the aqueous solution, when evaporated, left a white mass, from which urea was extracted by alcohol in so pure a state as to appear in crystalline tufts when the alcohol was evaporated.

The dialytic process is exceedingly well adapted to the separation of arsenious acid and other metallic poisons from liquids containing organic matter. Milk, defibrinated blood, and other organic substances, mixed with a few milligrammes of arsenic, and introduced into the dialyser floating on water, give up the greater part of the arsenious acid to the water in the course of 24 hours, and the diffusate is quite free from organic matter, so that the arsenic may be immediately precipitated by sulphydric acid and weighed as sulphide. [For further details, see LIQUIDS, DIFFUSION OF.]

**DIAMAGNETISM.** Many substances, *e. g.* bismuth, antimony, tin, cadmium, and gold, when brought near either pole of a powerful magnet, are repelled from that pole; and if a bar of such a substance be suspended between the poles of a horse-shoe magnet, or the opposite poles of two bar magnets, it places itself *equatorially*, or at right angles to the line joining the two poles. Such bodies are said to be diamagnetic, in contradistinction to magnetic bodies, like iron and nickel, which are attracted by the magnet, and place themselves *axially*, that is in the line joining two opposite poles. Diamagnetism does not, however, appear to be a distinct property of matter, the true explanation of the phenomenon being that all substances, including the air, are magnetic, and that the so-called diamagnetic substances are those which are less magnetic than the air, and consequently when brought near a magnetic pole, recede from it, just as a balloon recedes from the earth, because it is less attracted by the earth than an equal bulk of the surrounding air. (See MAGNETISM.)

**DIAMOND.** The purest form of carbon. It is almost always crystallised; rarely massive. The crystals belong to the regular system, exhibiting the simple forms  $O$ ,  $\infty O$ ,  $mO\infty$ ,  $mOn$  (figs. 149, 151, 186, 187) more rarely  $\infty O\infty$  and  $mO\infty$  (figs. 150, 183), and the combinations  $O \cdot \infty O\infty$  (fig. 161),  $O \cdot \infty O$  (fig. 199 &c.). The hemihedral forms of  $O$  and  $mOn$  likewise occur, the former especially in twin-crystals like fig. 321 (p. 160). Twins like fig. 319 are also found. The crystals usually have convex faces, the convexity being sometimes so great as to give them the appearance of rounded grains; they are often distorted and irregular, generally implanted singly, sometimes grown together in crystalline aggregates. Cleavage octahedral, perfect. Fracture conchoidal. The diamond has a specific gravity of 3.5 to 3.6, and its hardness (denoted by 10) is the highest known. It is colourless or white, tinged occasionally with yellow, red, orange, green, brown, or black; transparent, or, when dark-coloured, translucent. Its lustre is that known as adamantine. When rubbed, whether in the rough or polished state, it shows positive electricity. It becomes phosphorescent on exposure to the sun or the electric spark, and shines with a fiery light. In its power of refracting light it is exceeded only by red lead ore, and orpiment. Its index of refraction is 2.439. It reflects all the light falling on its posterior surface at an angle of incidence greater than  $24^\circ 13'$ , whence its great lustre is derived. Artificial gems reflect only the half of this light. Diamond is insoluble in all liquids, and infusible even before the oxy-hydrogen blowpipe; in the flame of the oxygen-blowpipe it burns away, producing carbonic anhydride, and leaving only a very trifling residue of ash. Sir H. Davy, in 1814, first showed that the diamond consists of pure carbon, by burning diamonds in an atmosphere of pure oxygen; and his conclusion has been confirmed by the experiments of Dumas and Stas (Ann. Ch. Phys. lxxvi. 1) and of Erdmann and Marchand (J. pr. Chem. xxiii. 169) made with larger quantities of diamond, and with attention to every condition necessary to ensure accuracy.

Diamonds are found chiefly at Minas Geraes in Brazil; in the Ural; in India, at Purlat between Hyderabad and Masulipatam, where the famous Kohinoor was found, also near Parma, in Bundelcund. A few also have been found in Borneo, in Georgia and North Carolina, and on the banks of the Turon in Australia.

The diamond appears generally to occur in regions which afford a laminated granular quartz-rock called *itacolomite*, which belongs to the talcose series, and owes its lamination to a little talc or mica; this rock occurs at the mines of Brazil and the Urals, also in Georgia and North Carolina. Diamonds have also been detected in a species of conglomerate composed of rounded siliceous pebbles, quartz, chalcedony, &c., cemented by a kind of ferruginous clay. At Minas Geraes in Brazil, the diamond is found in two different deposits; one called *gurgulho*, consisting of broken quartz and covered by a thin bed of sand or earth; the other, *cascalho*, of rolled quartz pebbles united by a ferruginous clay, resting usually on talcose clays, the whole being the debris of talcose rocks. The first deposit yields the finest diamonds, and both contain also gold, platinum, magnetic iron, rutile, &c.



The most highly valued diamonds are those which are colourless and perfectly transparent; but to give them the peculiar brilliancy for which they are chiefly prized, it is necessary to cut or grind them, in a peculiar way, so that the light falling on the gem in any direction may be perfectly reflected from one of its lower faces. A diamond may be split by a steel tool in the direction of the natural cleavages; but as this does not give the means of producing faces in any direction that may be required, it becomes necessary to resort to the process of abrasion, technically called "cutting." This is effected, either by rubbing two diamonds hard against each other, or by pressing the diamond against a rapidly revolving steel disc covered with diamond dust; this last method serves also for polishing. The dust for this purpose is obtained either in the process of abrasion, or by pounding rough diamonds, which are too opaque and highly coloured for gems, in a steel mortar. Such diamonds are called "bort." Diamond-dust is much used also for cutting and polishing other gems.

There are two forms given to cut diamonds, the brilliant and the rose. The rose is flat on the lower surface, while the upper portion is fashioned into a pyramid of twenty-four facets. The French brilliant consists of two truncated pyramids placed base to base: the upper portion, called the *pavilion* or *crown*, is half as thick as the lower, and terminates in a broad face, called the *table*, which has half the diameter of the entire stone and is surrounded by triangular and rhombic faces; the lower part of the brilliant, called the *culasse*, is pyramidal and terminates in a face having  $\frac{1}{2}$  the diameter of the stone. (For further details on these forms, and on the methods of cutting and polishing diamonds, see *Ure's Dictionary of Arts, Manufactures, and Mines*, ii. 21.)

The weight, and consequently the value of diamonds, is estimated in carats, one of which is equal to four grains; and the price of one diamond, compared to that of another of equal colour, transparency, purity, form, &c, is as the squares of the respective weights. The average price of rough diamonds that are worth working, is about £2 for the first carat. The value of a cut diamond being equal to that of a rough diamond of double weight, exclusive of the price of workmanship, the cost of a wrought diamond of

1 carat is		£8
2   "   "	$2^2 \times £8 =$	32
3   "   "	$3^2 \times 8 =$	72
4   "   "	$4^2 \times 8 =$	128
100   "   "	$100^2 \times £8 =$	80,000

This rule, however, is not extended to diamonds of more than twenty carats. The larger ones are disposed of at prices which cannot be reduced to any fixed rule. The snow-white diamond is most highly prized by the jeweller. If transparent and pure, it is said to be of the first water.

The hardness of the diamond renders it very useful for engraving and cutting glass. The sharp point of a natural diamond will scratch glass, but the cutting is effected by the curved edges formed by the intersection of the convex-faces; such an edge penetrates the substance of the glass like a wedge. Wollaston showed that rubies and sapphires ground so as to have curved edges will cut glass just like a natural diamond; only, being inferior in hardness, they wear out sooner.

The diamond is supposed to have been formed by the slow decomposition of some vegetable or bituminous material. Numerous attempts have been made to produce it artificially. Gannal supposed that he had obtained diamonds by decomposing sulphide of carbon with phosphorus. Recently, Despretz states that he has obtained microscopic octahedrons, having the hardness of diamond dust, by the prolonged action of an induction-current on sugar-charcoal; also by the action of an electric current continued for six months on one of the chlorides of carbon (not particularly specified); warty bodies are said to have been thus produced, nearly as hard as those just mentioned and exhibiting shining faces. Artificial diamonds, if they could be prepared at a moderate cost, would be very useful for the grinding and polishing of gems, glass, and other hard bodies. Diamond dust is found to give a finer edge to cutlery than can be obtained by the use of any other material. (Handw. 2<sup>e</sup> Aufl. ii. [3] 431.)

**DIANA.** The name applied by the older chemists and alchemists to silver; hence the dendritic amalgam precipitated by mercury from a solution of nitrate of silver was called *Arbor Diana*.

**DIANIC ACID.** Von Kobell's name for an oxide which he obtained from the tantalite of Tammela in Finland, the samarskite of the Ilmengebirg, and other similar minerals, and supposed to contain a metal different from tantalum and niobium. The oxide after boiling with water was said to be less soluble in water than tantalic or hyponiobic acid, and, when separated from its potash-solution, and treated with tin-



foil and hydrochloric acid in certain proportions, to form a dark blue liquid which became sapphire-blue on addition of a small quantity of water. According to H. Rose, Deville, and Damour, however, the so-called dianic acid does not differ essentially from the acids of niobium. Rose attributes the characters observed by Kobell to the presence of a small quantity of tungstic acid.

**DIANITE.** Von Kobell's name for the tantalite of Tammela in Finland.

**DIAPHANITE.** Syn. with DIPHANITE.

**DIAPHORITE.** Rhodonite or silicate of manganese mixed with quartz.

**DIASPORE.** *Laminated Hydrargyllite.*—Native monohydrate of alumina,  $\text{Al}^3\text{HO}^2$ , or  $\text{Al}^4\text{O}^2\cdot\text{H}^2\text{O}$ . Occurs crystallised in orthorhombic prisms, exhibiting the faces  $\infty\text{P}$ ,  $\infty\text{P}^3$ ,  $\infty\text{P}^4$ ,  $\infty\text{P}^\infty$ ,  $2\text{P}^2$ ,  $2\text{P}^\infty$  (Marignac and others). Inclination of  $\infty\text{P} : \infty\text{P} = 130^\circ 2'$  (Dufrénoy, *Compt. rend.* xxxi. 185);  $= 130^\circ 30'$  (Shepard, *Sill. Am. J.* [2] xii. 215);  $= 129^\circ 32'$  (Kengott, *Wien. Akad. Ber.* ix. 610);  $\text{P} : \text{P}$  in the brachydiagonal principal section  $= 151^\circ 25'$  (Dufrénoy);  $= 152^\circ 30'$  (Shepard);  $= 151^\circ 36'$  (Marignac, *Arch. Ph. nat.* vi. 296).  $\text{P} : \infty\text{P}$  in all directions  $= 125^\circ 17'$  (Dufrénoy);  $= 125^\circ$  (Shepard). Ratio of axes  $a : b : c = 0.8018 : 1 : 0.468$  (Marignac). The crystals are usually flattened prisms, sometimes acicular, commonly implanted. Cleavage very distinct parallel to  $\infty\text{P}^\infty$ ; less distinct parallel to  $\infty\text{P}^2$ . It occurs also foliated massive. Specific gravity 3.452 (Dufrénoy). Hardness  $= 6.5$  to 7. Colourless, yellowish, greenish, or bluish; transparent to sub-translucent. Lustre brilliant and pearly on the cleavage-planes; vitreous elsewhere. Very brittle. Gives off water when heated in a tube; is infusible before the blowpipe; turns blue when moistened with cobalt-solution and ignited. Not attacked by acids after ignition.

*Analyses.*—*a.* From Schemnitz in Hungary (Löwe, *Pogg. Ann.* lxi. 307); *b.* from Miask in Siberia (Hesse, *ibid.* xviii. 255); *c.* from Gumuch-dagh in Asia Minor (J. L. Smith, *Sill. Am. J.* [2] xi. 58); *d, e,* from Siberia (Dufrénoy, *Ann. Min.* [3] x. 677, 1837):

	$\text{Al}^4\text{O}^3$	$\text{H}^2\text{O}$	$\text{Fe}^2\text{O}$	$\text{Fe}^4\text{O}^3$	$\text{SiO}^2$	$\text{Ca}^2\text{O}$	$\text{Mg}^2\text{O}$	
<i>a.</i>	85.131	16.00	.	.	.	.	.	= 100.131
<i>b.</i>	85.44	14.66	.	.	.	.	.	= 100
<i>c.</i>	83.12	14.28	0.66	.	0.32	traces	traces	= 98.88
<i>d.</i>	78.93	16.13	0.52	.	1.39	1.98	.	= 97.95
<i>e.</i>	74.66	14.58	.	4.51	2.90	1.64	.	= 98.29

The formula  $\text{Al}^4\text{O}^3\cdot\text{H}^2\text{O}$  requires 85.1 alumina and 14.9 water.

Diaspore occurs in chlorite slate, near Koroibrod, district of Katherinenburg in the Ural, and at Schemnitz, in veins between dolomite and limestone; also at Broddbo, near Fahlun, Sweden; with corundum in dolomite at St. Gothard; at Gumuch-dagh and Mansen, Asia Minor, and in the Grecian islands Naxos, Samos, and Nicaria, with emery. (Dana, ii. 128.—*Jahresber. d. Chem.* 1847—8, p. 1163; 1860, p. 708; 1861, p. 763; 1865, p. 792; 1860, p. 763.)

**DIASTASE.** (Payen and Persoz, *Ann. Ch. Phys.* [2] liii. 73; lvi. 237; lx. 441; lxi. 351.—Guérin-Varry, *ibid.* lviii. 108; lx. 22; lxi. 22.—Bouchardat, *ibid.* [3] xiv. 61.)—The substance to which malt or germinated barley owes its property of converting starch into dextrin. It does not exist in all parts of the germinated grain being often absent in the radicles, and generally most abundant near the plumule. It exists in the tubercles of the potato near their points of insertion, but not in the roots or the shoots. It has also been found in the buds of *Ailantus glandulosa*. Neither potatoes nor cereals contain diastase before germination.

To extract diastase, malt is treated with water at  $25^\circ$  or  $30^\circ\text{C}$ ., which dissolves the diastase, together with an azotised substance. The solution is then heated to  $70^\circ\text{C}$ ., in order to coagulate the azotised albuminous substance, and the diastase is precipitated by absolute alcohol. It is purified by redissolving it in water and reprecipitating by alcohol. The proportion of diastase in malt does not exceed 0.002 to 0.003 per cent.

Diastase is a white amorphous substance, insoluble in absolute alcohol, soluble in water and in weak alcohol. Its aqueous solution is neutral to test-paper, has no decided taste, and is not precipitated by basic acetate of lead. Placed in contact with starch at  $70^\circ\text{C}$ ., it quickly disorganises that substance, and converts it, first into dextrin, then into glucose. According to Payen and Persoz, 1 pt. of well-prepared diastase is sufficient for the conversion of 2000 pts. of starch. The solution of diastase quickly alters, turning acid, and losing its power of converting starch. The same decomposition takes place, though slowly, in dry diastase; on boiling it with water, the decomposition is instantaneous.

Diastase has not been obtained in a state sufficiently definite for analysis. According

to Payen and Persoz, it contains less nitrogen the more carefully it has been prepared. According to Bouchardat, the conversion of starch into glucose may also be effected by contact with putrid flesh, beer-yeast, gastric juice, and animal membranes, which seems to imply that diastase is not a peculiar principle.

The action of diastase on starch is completely prevented by nitric, sulphuric, phosphoric, hydrochloric, oxalic, tartaric, or citric acid, also by caustic potash, soda, or lime, sulphate and acetate of copper, mercuric chloride, nitrate of silver, alum, and ferric sulphate. It is retarded more or less by formic acid, arsenious acid, magnesia, ammonia, and alkaline carbonates; slightly also by acetic acid, hydrocyanic acid, strychnine, quinine, morphine, and their salts. Essential oils, creosote, alcohol, and ether, exert no retarding influence. (Bouchardat.)

**DIASTASE, ANIMAL.** *Diastase salivaire*.—A substance precipitated from saliva by alcohol, and supposed to be the active fermenting principle of the saliva. It does not, however, convert starch into dextrin. (Mialhe.)

**DIASTASITE.** A black variety of amphibole from Nordmarken in Sweden.

**DIATEREBIC ACID.** See TEREBIC ACID.

**DIATHERMANOUS.** A term applied to bodies which transmit heat in the same manner as transparent bodies transmit light. (See HEAT.)

**DIAZO-COMPOUNDS.** See NITROUS ACID, SUBSTITUTION-PRODUCTS FORMED BY;—also OXY-ANISAMIC, OXY-BENZAMIC, OXY-CUMINAMIC, and OXY-TOLUYLAMIC ACIDS;—also PHENOL;—also PHENYL- and TOLUYL-DIAMINES.

**DICHROÏSM.** The property exhibited by many double-refracting crystals, of exhibiting different colours when viewed in different directions.

**DICHROÏTE.** *Cordierite*, *Iolite*, *Steinheilite*, *Hard Fahlunite*, *Sapphire d'eau*, *Peliom*, *Spanish Lazulite*.  $2\text{Mg}^2\text{O} \cdot \text{SiO}_2 + 2(\text{Al}^1; \text{Fe}^4)\text{O}^2 \cdot 3\text{SiO}_2 = \text{Mg}^4\text{SiO}^4 \cdot 3(\text{at} : \text{fe})^4\text{SiO}^4$ .—A mineral occurring in prisms, often hexagonal, belonging to the trimetric system;  $\infty\text{P} : \infty\text{P}_3 : \infty\text{P}_\infty$ ,  $\infty\text{P}$ , and sometimes other faces.  $\infty\text{P} : \infty\text{P} = 60^\circ 50'$ ;  $\infty\text{P}_\infty : \infty\text{P}_3 = 120 50'$ . Cleavage indistinct, parallel to  $\infty\text{P}$  and  $\infty\text{P}_\infty$ . Often in crystalline grains; also massive, compact. Specific gravity = 2.6–2.7. Hardness = 7.0–7.5. Colour bluish-white to blue, sometimes smoky blue (then called *pelion*); often deep blue along the principal axis, and brownish-yellow or yellow-grey at right angles to it. Streak uncoloured. Transparent or translucent. Fracture subconchoidal.

When heated it gives off a small quantity of water. Before the blowpipe it loses its colour, and melts with difficulty to a glass. It dissolves in borax and in phosphorus-salt, leaving in the latter case a skeleton of silica. It is but slowly attacked by acids.

*Analyses*.—1, 2, 3, Stromeyer (*Untersuchungen*, 329, 431.—4, 5, Schütz (Pogg. Ann. liv. 566).—6, Scheerer, *ibid.* lxxiii. 319, mean of two analyses).—7, Thomson (*Mineralogy*, i. 278).—8, S. Jackson (*Geol. Report of New Hampshire*, 184):

	SiO <sup>2</sup>	Al <sup>1</sup> O <sup>3</sup>	Fe <sup>4</sup> O <sup>3</sup>	Mn <sup>2</sup> O	Mg <sup>2</sup> O	Ca <sup>2</sup> O	K <sup>2</sup> O	H <sup>2</sup> O
1. Bodenmais . . .	48.35	31.70	9.24	0.33	10.16	0.59	. . .	=100.37
2. Greenland . . .	49.17	33.10	4.82	0.04	11.45	. . .	. . .	1.20 = 99.78
3. Fahlun . . .	50.25	32.42	4.45	0.76	10.85	. . .	. . .	1.66 = 100.39
4. Ostgothland . . .	48.6	30.5	11.9	0.1	8.2	. . .	. . .	1.5 = 100.8
5. Südermannland . . .	49.7	32.0	6.7	0.1	9.5	. . .	. . .	2.1 = 100.1
6. Kragerö . . .	50.44	32.95	1.07	. . .	12.76	1.12	. . .	1.02 = 99.36
7. Haddam, Conn. . .	49.62	28.72	12.86	1.51	8.64	0.23	. . .	=101.58
8. Unity, Maine . . .	48.15	32.50	8.80	0.28	10.14	. . .	. . .	0.50 = 100.37

Dichroïte occurs in granite at Cabo de Gata in Spain, at Arendal in Norway, at Orijervi in Finland (*Steinheilite*), at Tunaberg in Sweden, and other localities; in quartz at Ujordlersoak in Greenland, in gneiss at Haddam, Connecticut, and Brinfield, Massachusetts. The smoky blue variety called *pelion* is found at Bodenmais in Bavaria, sometimes in perfect crystals  $1\frac{1}{2}$  inch thick. Dichroïte is sometimes used as a gem. A transparent variety, called *Sapphire d'eau* by jewellers, is found in small rolled masses of deep blue colour in Ceylon. (Dana, ii. 214; Rammelsberg, p. 766.)

*Hydrous Dichroïte*.—Dichroïte alters so readily by exposure that it is commonly found in the altered state, or as a nucleus enclosed in a crust of the altered mineral. The change consists either in a simple hydration, as in *Bonsdorffite* from Abo, *Esmarkite* from Brevig in Finland, *Chlorophyllite* from Unity in Maine and Haddam in Connecticut, and *Prasecolite* from Bräkke in Norway,—or in the removal of part of the protoxides by carbonic acid,—or the introduction of oxide of iron through carbonate of iron, or of alkalis through waters containing alkaline carbonates.

The composition of the hydrous dichroites formed by simple hydration, is as follows:

	SiO <sup>2</sup>	AlO <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	Mg <sup>2</sup> O	H <sup>2</sup> O	Mn <sup>2</sup> O	
Bonsdorffite	45.05	39.05	5.30	9.00	10.60	trace	= 100
Chlorophyllite	45.20	37.60	8.34	9.60	3.60	P <sup>2</sup> O <sup>5</sup> trace	= 99.32
Kemurkite	45.97	32.08	3.83	10.32	5.49	Ca <sup>2</sup> O, Pb, Cu, Co, Ti 0.45	= 98.55
Praseolite	40.94	28.79	6.96	13.73	7.38	Pb <sup>2</sup> O, Cu <sup>2</sup> O, Co <sup>2</sup> O, Ca <sup>2</sup> O 0.80	= 98.63

Denoting dichroite by D, bonsdorffite = D + 3aq.; chlorophyllite = D + aq.; esmarhite = D + 1½aq.; praseolite = D + 1½aq. (Dana, ii. 215). See also ASPASIO-LITE, FAHLUNITE, GIGANTOLITE, HURONITE, IBERITE, LIEBENERITE, PINITE, PYRROIL-LITE, WEISSITE.

**DI-COMPOUNDS.** In this Dictionary, the syllable *di*, prefixed to the name of a radicle occurring in any compound, denotes that the compound in question contains two atoms of that radicle; *e. g.* di-chloride of tin = SnCl<sub>2</sub>; di-oxide of tin = SnO<sub>2</sub>; di-sodic phosphate = Na<sup>2</sup>HPO<sub>4</sub>; di-ethylamine = N.H.(C<sup>2</sup>H<sub>5</sub>)<sub>2</sub>; di-ethylenic alcohol = (C<sup>2</sup>H<sub>4</sub>)<sub>2</sub>.H<sup>2</sup>O<sub>2</sub>. The prefix *bi* is often used in the same sense. (See NOMENCLATURE.)

Individual di-compounds are described under the several general headings, *e. g.* Dichloride of Tin, under TIN, CHLORIDES OF; Disodic Phosphate, under PHOSPHATE OF SODIUM; Diethylamine, under ETHYLAMINE, &c.

**DICTAMNUS ALBUS.**—The root of this plant, which is the only European species of *Diosmea*, was formerly used as a vermifuge; it is resinous, bitter, and aromatic; the root-bark was said to be peculiarly efficacious.

**DIDRIMITE or DIDYMIT.** A mineral from the Zillerthal in the Tyrol, having the aspect of microcrystalline tale. Specific gravity = 2.75. Contains 40.69 per cent. silica, 18.15 alumina, 22.74 lime and carbonic anhydride, 11.16 potash, 1.2 soda, 5.25 ferric oxide, and 0.60 water. (Kengott, Handw. d. Chem. 2<sup>e</sup> ausf. ii. [3] 437.)

**DIDYMIUM.** Symbol Di. Atomic weight 48.—This metal, discovered by Mosander in 1841 (Pogg. Ann. lvi. 504), exists, together with cerium and lanthanum, in cerite, allanite, orthite, ytrocercite, cryptolite, and a few other minerals (i. 831); it is not found in nature in the free state, or even as a pure oxide, sulphide, or other compound, but always associated with cerium and lanthanum. Its compounds greatly resemble those of lanthanum, and are very difficult to separate therefrom: hence the name didymium (from *δίδυμος*, twin). The compounds of didymium have been investigated by Mosander (*loc. cit.*), Watts (Chem. Soc. Qu. J. ii. 131), more especially by Marignac (Ann. Ch. Phys. [3] xxvii. 209; xxxviii. 148), and recently by R. Hermann (J. pr. Chem. lxxxii. 385).

A pure salt of didymium is obtained by recrystallising the rose-coloured rhombohedrons which separate from an acid solution of the mixed sulphates of lanthanum and didymium by spontaneous evaporation (see LANTHANUM); and from the pure sulphate thus prepared, the other compounds of the metal may be formed.

*Metallic didymium* is prepared by heating potassium with an excess of chloride of didymium, and washing out the soluble chlorides with cold water. It is thus obtained, for the most part, as a grey metallic powder, but partly, also, in fused globules. The powder, thrown into the flame of a spirit-lamp, burns with bright sparks like iron-filings. The powder decomposes water at ordinary temperatures; the fused granules do not: in either form, however, the metal dissolves rapidly in dilute acids with evolution of hydrogen.

But few of the compounds of didymium have yet been examined. It forms a protoxide, Di<sup>2</sup>O, and a protochloride, DiCl, and a class of oxygen-salts of corresponding composition.

**DIDYMIUM, CHLORIDE OF,** DiCl, is obtained as a hydrate in rose-coloured crystals of considerable size by evaporating a solution of the oxide in hydrochloric acid. The crystals, which are very soluble in water and alcohol, contain DiCl.2H<sup>2</sup>O. The solution, when evaporated, gives off hydrochloric acid, and leaves an oxide, not however of constant composition (Marignac). According to Hermann it leaves an oxychloride.

**DIDYMIUM, DETECTION AND ESTIMATION OF.** The salts of didymium have either a pure rose-colour, like the sulphate, or slightly inclining to violet, like the nitrate in the state of strong solution. Potash, soda, and ammonia precipitate the hydrate; so does sulphide of ammonium. Carbonate of barium also throws down the hydrated oxide slowly, but completely. Oxalate of ammonium precipitates didymium completely from neutral solutions; and oxalic acid almost completely, unless the solution contains a large excess of acid. The sulphates of potassium, sodium, and ammonium form, immediately in strong, and gradually in weak



solutions, rose-white precipitates of double sulphates, slightly soluble in water, less soluble in excess of the reagent; the sodium-salt is the least soluble of the three. *Phosphoric and arsenic acids*, at a boiling heat, form precipitates sparingly soluble in acids. All compounds of didymium impart to *borax* and *phosphorus-salt* a very pale rose-colour. They do not colour carbonate of sodium before the blowpipe.

According to Gladstone (Chem. Soc. Qu. J. x. 319), didymium-salts are easily recognised in solution by spectral analysis. When a ray of light, after passing through such a solution, is examined by a prism, it is found that the violet rays are completely absorbed by a solution of nitrate of didymium, but not by the chloride or sulphate. All three solutions, however, form a spectrum containing two black lines, inclosing a very bright portion of the spectrum. One of these black lines is in the yellow immediately following Fraunhofer's line D; the other is situated between E and *b*. These characters can be distinctly recognised in a solution half an inch deep, containing only 0.01 per cent. of didymium-salt.

*Quantitative estimation of Didymium.*—Didymium is precipitated from its solutions by potash, and the precipitate is converted by ignition in a covered platinum crucible into the anhydrous protoxide, containing 85.7 per cent. of the metal.

The methods of separating didymium from other metals are the same as those adopted for cerium. The separation of didymium from cerium itself may be effected by boiling the mixed oxides in a solution of sal-ammoniac (Watts). For separating didymium from lanthanum, no method has yet been devised sufficiently accurate for quantitative analysis.

*Atomic weight.*—Marignac in 1848 determined the atomic weight of didymium by the quantity of chloride of barium required to precipitate a given weight of the sulphate; in this manner he obtained the number 49.6. Afterwards, in 1853 (Ann. Ch. Phys. [3] xxxviii. 148), he found that this method was inexact, because the precipitated sulphate of barium carried down with it a quantity of didymic sulphate, which was not afterwards decomposed by excess of chloride of barium. He therefore adopted two other methods: 1. By precipitating the didymium from the sulphate by oxalate of ammonia, igniting the precipitate till it turned white, and weighing the protoxide thus obtained.—2. By precipitating the chloride of didymium with nitrate of silver, estimating the chlorine as chloride of silver, and precipitating the didymium from the filtrate in the manner just mentioned. The mean of the experiments made by the first method gave for the atomic weight of didymium, on the oxygen-scale, the number 598.2; the second method gave 603.5, 598.9, and 598.3. Mean of the whole, 599 on the oxygen-scale, or 47.92 on the hydrogen-scale. Marignac considers the number 48 to be very near the truth. Hermann by igniting the oxalate obtains the number 47.48.

**DIDYMIUM, OXIDES OF.** Didymium forms two oxides, the protoxide,  $\text{Di}^{\circ}\text{O}$ , and a peroxide, whose atomic constitution is not exactly known.

The *protoxide* is obtained in the anhydrous state by strongly igniting the nitrate, oxalate, or the precipitated hydrate, in a covered crucible. It is perfectly white; is slowly converted into a hydrate by immersion in warm water; dissolves readily in the weakest acids; and expels ammonia from ammoniacal salts when boiled with them.

The hydrate,  $\text{DiHO}$ , is a gelatinous mass, resembling hydrate of alumina, but having a very pale rose colour. It contracts much by desiccation.

*Peroxide of Didymium.*—When the oxalate, nitrate, carbonate, or hydrate of didymium is ignited in contact with the air, and not very strongly, a dark brown oxide is obtained, containing from 0.32 to 0.88 per cent. of oxygen more than the protoxide. When treated with acids it dissolves readily, giving off the excess of oxygen, and forming a solution containing the protoxide. It is probably a mixture of the protoxide with a small quantity of a higher oxide of definite composition. By strong ignition in a close vessel, it is converted into the white protoxide. (Marignac.) According to Hermann, it contains  $\text{Di}^{\circ}\text{H}^{\circ}$ .

**DIDYMIUM, SULPHIDE OF.**  $\text{Di}^{\circ}\text{S}$ , is obtained by igniting the oxide in the vapour of sulphide of carbon. It is a light brownish green powder, which dissolves in acids, with evolution of sulphydric acid. A greyish-white *oxysulphide*,  $\text{Di}^{\circ}\text{O}^{\circ}\text{S}$ , or  $\text{Di}^{\circ}\text{S} \cdot 2\text{Di}^{\circ}\text{O}$ , is obtained by igniting the oxide with carbonate of sodium and excess of sulphur, and digesting the fused mass in water. (Marignac.)

**DIFFLUAN.** (Schlieper, Ann. Ch. Pharm. lvi. 5.)—A compound formed, together with leucoturic acid, &c., when an aqueous solution of alloxanic acid is boiled for some time. (See ALLOXANIC ACID.) It separates on the addition of alcohol to the aqueous solution, and must be collected on a filter out of contact with the air, washed with alcohol and ether, and dried in vacuo over sulphuric acid. It is not crystallisable, but forms a loose white powder of a bitter saline taste, and reddens litmus strongly. It is very soluble in water, and deliquesces rapidly in the air: insoluble in alcohol. When heated it melts at  $100^{\circ}\text{C}$ ., giving off alcohol and water with intumescence, and

remains as a transparent vitreous gum, which may be rubbed to a white powder. It is decomposed with effervescence by hot nitric acid, forming alloxan. It is gradually decomposed by cold potash, ammonia being evolved, and oxalic acid formed abundantly. Its aqueous solution gives white precipitates with nitrate of silver and acetate of lead, the latter soluble in excess of the lead-solution.

The composition of this body is not accurately known. Schlieper assigns to it the formula  $C^8H^{10}N^2O^3$ , relying on an analysis which gave 32.69 per cent carbon, 3.89 hydrogen, and 25.70 nitrogen (calculation 33.33 C, 3.70 H, 25.53 N, 37.04 O).

The silver-precipitate gave on analysis 45.5 per cent. oxide of silver, which does not accord with Schlieper's formula. Laurent (Compt. rend. xxxv. 629) gives it the formula  $C^8H^{10}N^2O^3$ , regarding it as isomeric with dialuramide. Gmelin points out that, since alloxan is obtained from it, it probably contains 4 atoms of carbon. F. T. C.

**DIFORMENE** or **BIFORMENE**. Lallemand's name for the hydrocarbon  $C^8H^8$ .

**DIFFUSION**. The mixing or mutual interpenetration of two liquids or gases which do not unite chemically one with the other. This kind of mixture takes place both when the fluids are in immediate contact, and when they are separated by porous membranes or other partitions. (See GASES and LIQUIDS, DIFFUSION OF).

**DIGENITE**. A variety of copper-glance from Sangerhausen in Thuringia and from Chile. Specific gravity = 4.568 to 4.68. Hardness = 2.0. Plattner found in it 70.2 per cent. copper and 0.24 silver, which approximates to the formula  $Cu^{18}S^4 = Cu^3S.3Cu^2S$ , or 1 atom copper-glance and 3 atoms purple copper.

**DIGESTER** or **DIGESTOR**. An apparatus for digestion, such as a sand or water-bath. *Papin's digester* is a strong iron vessel in which substances can be exposed to the action of water or other liquids at temperatures above their boiling points.

**DIGESTION**. The operation of exposing a substance to the action of a liquid with the aid of heat, generally below the boiling point of the liquid, for the purpose of extracting the soluble constituents. The treatment of a substance with a cold liquid is called *maceration*.

**DIGESTION, ANIMAL**. (Lehmann, *Lehrbuch der Physiologischen Chemie*, Leipzig 1853, iii. 216-283.—The same translated by Dr. Day, London 1854, iii. 248-324.—Gmelin's *Handbuch*, viii. 672-621.—Frerichs, *Die Verdauung. Handwörterbuch d. Physiologie*, Braunschweig, 1846, iii. 1.—Bidder and Schmidt, *Die Verdauungssäfte und der Stoffwechsel*, Mitau und Leipzig, 1852.—Marcet, *On the Chemistry of Digestion*, Chem. Soc. J. xv. 407.)

The changes which food undergoes in the stomach and intestines consist essentially in its transformation either into soluble substances, or into emulsions, whereby it is rendered capable of passing into the blood-vessels and lacteals, and available for the purpose of nutrition. These changes are produced by the action of the saliva, gastric juice, bile, pancreatic juice and intestinal juice, fluids which are poured from time to time into the alimentary canal in very large quantities, amounting in twenty-four hours, according to the experiments of Bidder and Schmidt, to almost the sixth part of the weight of the body. If the results obtained by these physiologists from experiments on animals can be applied to man, it may be calculated that a man weighing 64 kilogrammes (or about 10 stone) will secrete in twenty-four hours:

Saliva amounting to 1.6 kilogrammes, containing 15 grms. of solid matter.					
Bile	1.6	"	"	80	" "
Gastric juice	6.4	"	"	192	" "
Pancreatic juice	0.2	"	"	20	" "
Intestinal juice	0.2	"	"	about 3	" "

The chief function of the *pancreatic juice* and, in some cases, of the *saliva*, is the conversion of starch into dextrin and sugar: according to Bernard (*Leçons de Physiologie expérimentale appliquée à la Médecine*, Paris, 1856, ii. 170-453), the *pancreatic juice* also assists in decomposing neutral fats into glycerin and fatty acids; and this view is now generally admitted, although it is opposed to the results obtained by Frerichs and by Bidder and Schmidt. The *gastric juice* is the chief agent by which the albuminous or protein substances are rendered soluble; according to Marcet, it likewise converts the neutral fats into fatty acids. The *bile*, according to the same authority, converts into an emulsion the fatty acids thus produced. The *intestinal juice* appears to unite in itself, to a certain extent, the functions of the gastric and pancreatic fluids, having the power of rendering soluble both starch and flesh, or other protein-bodies.

The albuminous or protein-substances, *albumin*, *fibrin* and *casein*, both animal and vegetable, are, so far as their chemical composition is concerned, ready for immediate



assimilation by the animal body; in fact they do not undergo any chemical change in the process of digestion; but, under the influence of the gastric juice, they lose their coagulability by heat and by mineral acids, and likewise their property of forming insoluble combinations with most metallic salts, and are converted into soluble isomeric modifications of albumin, fibrin and casein, called by Lehmann peptones. In this state they are fit to be taken up by the absorbents. The conversion of these bodies into peptones is not, however, completed in the stomach, a large portion of the albuminous constituents of the food passing unaltered into the intestines, where their conversion into peptones is completed by the action of the intestinal juice. Indeed the quantity of gastric juice secreted is not sufficient to effect the solution of the protein-matters required for nutrition. A dog secretes about 100 grammes of gastric juice in twenty-four hours for every kilogramme's weight of its body (Bidder and Schmidt), and this quantity of gastric juice is capable of digesting about 5 grammes of albumin, reckoned as dry (Lehmann); but it appears from Schmidt's experiments, that a dog, to keep in condition on an exclusively flesh diet, should take, for every kilogramme's weight of its body, 50 grammes of flesh containing 10 grammes of dry albuminoids: hence the gastric juice secreted by the dog would only suffice for the digestion of half of the albuminoids necessary for its nutrition. That the intestinal juice is capable of digesting these bodies is proved by the experiments of Bidder and Schmidt, who found that pieces of flesh and coagulated albumin introduced into tied loops of intestine were digested in from 6 to 14 hours; also that the pure alkaline intestinal juice, as well as that secretion mixed with bile and pancreatic juice, possesses the power of dissolving protein-substances externally to the body. The transformation of the carbohydrates by the intestinal juice appears to take place wholly in the small intestine.

*Gelatin* and the gelatigenous tissues in general are converted in the stomach into substances which, according to Lehmann, correspond perfectly, in their physical and in most of their chemical properties, with the peptones of the protein-bodies. According to Marcet, however, the peptones produced from gelatinous tissue differ in some of their physical properties from those derived from the protein-bodies, especially in their action on polarised light. Pure gastric juice obtained by washing out the stomach of a dog with water, after it has been kept fasting for thirty hours, and then making the animal swallow pebbles, is quite destitute of optical rotatory power; so likewise is the solution of pure albumin or casein in this gastric juice; but if the dog be then fed with cartilage, a gastric juice is obtained possessing considerable lavo-rotatory power (see GASTRIC JUICE).

Many nitrogenous substances undergo decomposition in passing through the stomach and intestines—such, for example, is the case with *emulsin*. We know that when this substance acts upon amygdalin (i. 201), in presence of water, prussic acid is produced, and accordingly, when emulsin and amygdalin are introduced together into the stomach or into the blood, the animal dies with the symptoms of poisoning by prussic acid. Lehmann allowed rabbits to eat sweet almonds (which contain emulsin) and injected amygdalin into the jugular vein, one, two, four, and six hours after they had been fed; the animals remained perfectly vigorous, showing that the emulsin had not been absorbed into the circulation; but on reversing the experiment, and injecting emulsin into the vein and introducing a solution of amygdalin into the stomach, symptoms of poisoning by prussic acid soon showed themselves. In the former case, then, either the emulsin had been metamorphosed by the digestive fluids, or it was incapable of being taken up by the absorbents. To decide this point, Lehmann collected the excrements of a rabbit which had been fed for forty-eight hours on almonds, and mixed amygdalin with them, but could detect no trace of prussic acid; neither was any decomposition of the amygdalin induced by the caecal contents of the same animal: hence he infers that the emulsin was decomposed in the intestine.

*Curarine*, the poison of serpents, and those poisons which are produced in contagious diseases, as *hydrophobia*, *glanders*, *typhus*, &c., are likewise decomposed in passing through the stomach and intestines: all these substances may be taken with impunity into the alimentary canal, but produce fatal or at least morbid effects when introduced into the blood.

The mode of digestion of the *neutral fats*, such as are contained in butter, the fat of meat, olive oil, &c., has been the subject of much controversy. The generally received opinion is that these bodies do not undergo any alteration, either mechanical or chemical, by the action of the saliva or the gastric juice, but that their digestion commences in the duodenum, in passing through which, and still more in its further passage through the jejunum and ileum, the fat ceases to appear in large drops or semifluid masses, these drops becoming smaller and smaller as the fat descends in the small intestine, till at length it appears finely comminuted, and is, in fact, converted into an emulsion, a



condition which greatly facilitates its absorption by the lymphatics of the intestinal walls. The mere mechanical division of the fat is not, however, the only condition necessary for its absorption. Bidder and Schmidt have shown that bile is essential to the digestion of fats, and Wistinghausen (*Dissert. inaug.* Dorpat, Livon. 1851) has ascertained that oil cannot be made to penetrate through animal membranes without considerable pressure, but that it may be forced through with comparative ease when the membrane is saturated with a fluid which adheres to or has an affinity for the oil. When the membrane was moistened with a solution of potash, an abundance of saponified oil passed through it in the course of ten hours, under a very slight pressure (from 0.068 to 0.132 of an inch of mercury), and associated with it was free fat mechanically carried through by the soap. When a mixture of equal parts of potash-ley and albumin was used, the oil passed through the membrane, even without pressure, although in very small quantity; in this case also a soap was formed. The oil, however, passed through animal membranes without being saponified when they were saturated with a solution of soap or bile.

Marcet takes a different view of the digestion of neutral fats. He infers from his own experiments, that these fats are resolved into glycerin and fatty acids in the stomach, and are then transformed into emulsions by the action of the bile, which exerts this action upon fatty acids, but not on neutral fats. Fatty acids are altogether much more capable of forming emulsions than neutral fats. When neutral fats or fatty acids in a fused condition are agitated with water, no emulsion is formed, but large globules are seen to pervade the fluid; on standing, they immediately run into each other, and rise to the surface, the aqueous fluid remaining perfectly clear. When fused neutral fats are agitated with a solution of neutral trisodic phosphate, the same phenomenon takes place as with pure water, but when fused fatty acids are shaken in a test-tube with phosphate of sodium, or with bile, the fat is instantly divided by a mechanical process into very minute globules, just as would happen if the fat were agitated with water; but at that moment each of these very small fatty particles becomes surrounded with a layer of soap, from the surface of the globule being saponified by the sodic phosphate or the bile. From this circumstance the globules of fat lose their property of running into each other, and acquire a slight increase of specific gravity, which, however, is not sufficient to prevent them from rising slowly in the mother-liquor, and finally occupying the upper part of the liquid. Thus it is that the fluid is milky, and that the emulsion takes a much longer time to rise to the surface than pure oil would. The chemical analysis of the emulsion bears out this view, for it is found to consist invariably of free fatty acid and soap.

These facts will assist in explaining the absorption of fats, since, when in the form of an emulsion, they can no longer be in direct contact with the intestines, a layer of soap intervening between the fat and the membrane. Soaps may be conceived to pass through a membrane, whilst fat is known to be incapable of so doing; consequently we may imagine fats to be absorbed under the form of complex globules, the inside of which is free fat, and the outside soap.

These observations on the power of bile to convert fatty acids into an emulsion and afterwards into soap, are quite in accordance with the results obtained by Bidder and Schmidt, and by Wistinghausen above mentioned, though it does not appear that these observers noticed the difference existing in this respect between neutral fats and fatty acids.

The power of digesting fats does not, however, belong exclusively to the bile: for a portion of the fats taken into the stomach is not acidified, and consequently must escape the action of the bile; in this case, the pancreatic juice effects the conversion, as observed some time ago by Bernard. The absorption of fatty acids explains a fact observed by Verdeil and Marcet in 1851, viz. that the blood contains free fatty acids.

Among the so-called *carbo-hydrates*, the most important as an article of food is *starch*. This substance, being insoluble, cannot be taken up by the absorbents until it has been converted into dextrin and sugar, a change which is effected partly by the saliva, partly by the pancreatic and intestinal juices. The action of saliva upon starch is not the same in all animals. Odling found that pure parotid saliva, obtained from a man who had a fistulous opening in the parotid duct, converted boiled starch quickly, and raw starch more slowly, into sugar, whereas saliva obtained in like manner from a young donkey had no effect on starch, either boiled or unboiled. According to Bernard, the saliva of horses is likewise without action on starch. In ruminating animals, which retain their food for a long time in the paunch, where it is exposed to the continuous action of the saliva, a great portion of the starch contained in the food is probably transformed into sugar; and the same is the case in the crop of birds; but in all other animals, the action of the saliva during the short time that the food remains in the mouth, must be very slight, so that the greater part of the starch passes unchanged into the stomach, where the further action of the saliva upon it is

to a certain degree suspended by the gastric juice, when secreted in sufficient quantity. On passing into the duodenum, the starch is brought in contact with the powerfully acting pancreatic juice, and afterwards in the ileum, with the intestinal juice, which acts upon it in a similar manner, but less strongly. As the starch passes on, the granules become softened on their surface, diminish in size, and are gradually dissolved in the form of dextrin and glucose; the dextrin is the first product of the transformation, but is so rapidly converted into sugar, that it is rarely found in the intestine, and even then only in very small quantity.

*Inulin* is affected by the digestive fluids in the same manner as starch; but, according to Lehmann's experiments, its transformation is much more rapid.

*Glucose* or *grape-sugar*, whether formed from starch in the manner above described, or introduced directly into the alimentary canal, is partly taken up directly by the intestinal absorbents, and passes into the blood without alteration, and is partly converted, by the action of the bile and intestinal juices, into lactic acid, and in that state passes into the circulation. *Cane-sugar* appears to be converted into glucose before it is absorbed into the circulation. *Milk-sugar* appears to comport itself in the intestinal canal in the same manner as glucose; it distributes itself very rapidly throughout the small intestine, and in about an hour after it has been swallowed, may be traced as far as the cæcum; but, like glucose and cane-sugar, it occasions an intensely acid reaction in the jejunum and ileum, which remains for three or four hours after the injection of the sugar.

*Pectin* and the allied substances are totally unaffected by the digestive fluids. (Blondlot, Frerichs.)

*Gum*, although an easily soluble substance, does not play an important part in the process of animal nutrition; indeed it rarely occurs as a constituent of nutritive matters, even of the food of the herbivora. It is not affected by the digestive fluids, and, when given to animals, is not subsequently found in the blood or in the urine, but passes unchanged into the solid excrements. Boussingault caused a duck to swallow fifty-two grammes of gum-arabic, and in the course of nine hours forty-six grammes were recovered from the excrements. The fact of gum not being taken up in perceptible quantity by the intestinal absorbents, is related to its low diffusibility, which, according to Graham, is only half that of starch-sugar, and four or five times less than that of chloride of sodium.

*Cellulose*, or *woody-fibre*, resists the action of all the digestive fluids: hence all vegetable substances essentially consisting of cellulose pass unchanged into the excrements of most herbivorous and omnivorous animals. In some animals, however, which swallow very large quantities of woody fibre, it appears probable that some means must exist of rendering this substance soluble. In the beaver, the whole stomach, and more especially the cæcum, are often found plugged, as it were, with fragments of wood and bark, amongst which, according to Lehmann, no easily soluble nutrient substance can be detected. Now, in this animal, the organs whose secretions contribute more especially to the metamorphosis of the carbo-hydrates, are developed in a remarkable degree—the salivary glands amounting, according to Weber, to  $\frac{1}{11}$  of the whole weight of the body, whereas in man they do not exceed  $\frac{1}{80}$  of the entire weight. The pancreas in the beaver is also very bulky, and there is a large gastric gland, peculiar to the animal, which may perhaps have some relation to its power of digesting cellulose. It is well known that cellulose is converted into dextrin, or a similar substance, by the action of alkalis, even when very dilute—and it is by no means improbable that the alkaline juices of the salivary glands, the pancreas, and the caecal glands of the beaver may effect this transformation.

The relative digestibility of different kinds of food is a subject on which it is very difficult to obtain precise results, inasmuch as the facility with which any substance is digested depends very much on its state of mechanical division or aggregation, and on the condition of the digestive organs at the time when the food is taken; food taken into the empty stomach, after fasting for some hours, will be digested much more quickly than the same kind of food introduced into the stomach partly full or immediately after it has been emptied. The point to which observation has been chiefly directed is the time during which different kinds of food remain in the stomach, those being considered the most digestible which pass out most quickly, in intervals varying from an hour to an hour and a half. Such observations are made either by feeding animals with different kinds of food, and killing them at various intervals after the meals—or by introducing portions of food enclosed in muslin bags into the stomachs of animals bearing gastric fistule. A series of observations of this latter kind were made by Beaumont (*Experiments and Observations on the Gastric Juice and Physiology of Digestion*, Boston, 1834), on a man having a large fistulous opening into the stomach resulting from a gun-shot wound. It is clear, however, that such observations can give but an imperfect idea of the relative digestibility of different articles of food,

inasmuch as the digestion, even of albuminous substances, is not completed in the stomach, and that of most vegetable substances does not even commence till they reach the intestine.

The digestibility of the *albuminous bodies* depends very much on their state of aggregation. Soluble coagulable *albumin*, like unboiled white of egg, is much more digestible than the same substance when coagulated. Soluble *casein*, as it exists in milk, is one of the most indigestible of the unboiled albuminous substances, inasmuch as it is very quickly coagulated by the acid gastric juice, and then but slowly dissolved. A considerable difference is, however, observable, according to the denser or more porous condition of the coagulum. The casein of human milk, which forms a gelatinous coagulum, is much more rapidly digested than that of cows' milk, which forms in the stomach a compact lump, generally coagulated into a solid ball.

*Syntonin*, or *muscle-fibrin*, is, according to Lehmann, very easily digested, more easily than the blood-fibrin of the ox. The digestibility of muscle varies, however, greatly with its conformation. The smooth muscular fibre, like that of the stomach and intestines, is much more digestible than the striated muscles, because the former is not provided with the dense and insoluble, although thin integument, which encloses the primitive bundles, and consequently the syntonin, in the latter,—but is for the most part surrounded only by loose connective tissue, which is easily permeated and dissolved by the digestive juices. The flesh of young animals is more easily digestible than that of older animals, because the primitive bundles of the former are much thinner than those of the latter, and consequently present, in relation to their mass, a larger extent of surface to the action of the gastric juice. Frerichs found that the flesh of old animals required for digestion an hour or an hour and a half longer than that of young animals.

Raw flesh is generally regarded as more difficult of digestion than boiled or roast meat; the difference is not, however, very great, and has been estimated by Frerichs at only half an hour. In fact, the advantage derived from the loosening of the connective tissue and the partial destruction of the organic structure by boiling or roasting, is partly counteracted by the coagulation of the albumin in the muscular juice and the hardening of the syntonin.

*Gelatin*, in its pure state, is one of the most easily digestible substances. In Beaumont's experiments, the gelatinous character of this substance disappeared after it had remained twenty minutes in the stomach, and after an hour no trace could be found of 120 grammes of jelly which had been taken. The digestibility of the *gelatigenous tissues* depends, however, very much upon their state of aggregation, and is greatly increased by boiling. Tendons and cartilage, and all those tissues which are abundantly intersected with elastic fibres, belong to the least easily digested class of substances, inasmuch as true elastic tissue and elastic fibres completely resist the action of the digestive fluids.

The *fats* belong to the least digestible class of substances; indeed fat, when taken in large quantity, either alone or with other food, usually remains for a long time in the stomach, sometimes even for 6½ hours. It is not only not digested in the stomach, but often exerts an impeding action on the digestion of other substances, since it is liquefied by the heat of the stomach, and, encasing the particles of food, prevents them from coming in contact with the gastric juice; moreover, it becomes rancid during its long retention in the stomach, and forms volatile acids, which exert a very deleterious, though not well understood action on digestion. The true digestion, that is, the emulsification of fat, does not, indeed, commence till it reaches the small intestine, where it comes in contact with the bile (p. 325). Small quantities of fat appear, however, to be easily digested; and, according to Lehmann, fat, when not mixed in too large quantity with the food, essentially promotes the digestion both of albuminous and amylaceous substances.

*Starch*, the principal nutrient matter of most vegetable food, is much more easily digested in the boiled than in the raw state, the effect of the boiling being to burst the envelopes of the starch-granules and thus expose the starch to the action of the saliva and the pancreatic and intestinal juice, whereby it is converted into sugar. When raw starch is eaten in large quantity, a considerable portion of it passes away unchanged in the solid excrements.

The digestibility of *vegetables* depends very much on the nature of the cells in which the starch and the albuminous matters are enclosed; if the cells are still invested with epidermis, no portion of them is dissolved, the epidermis of plants being completely proof against the digestive fluids. Boiling usually renders vegetable food more digestible, by thoroughly loosening the intercellular substance, and thus allowing the digestive juices to make their way more readily into the cells.

**DIGESTIVE SALT.** *Sal digestivum Sylvii.* Syn. with CHLORIDE OF POTASSIUM.



**DIGESTOR.** See DIGESTER (p. 323).

**DIGITALACRIN.** *Digitalicin.* This name was applied by Walz (Jahrb. pr. Pharm. xxi. 29) to an acid substance which he obtained from crude digitalin by exhaustion with ether, and to which he assigned the formula  $C^{22}H^{20}O^6$ . Subsequently this product has been found to be a mixture of several substances. When its alcoholic solution is mixed with basic acetate of lead, which takes up the colouring matter, the filtrate evaporated, and the residue washed, first with ammoniacal water, then with cold alcohol, and dissolved in boiling alcohol, white nacreous laminae are obtained, consisting of Walz's digitaloic acid  $C^{22}H^{22}O^6$ , soluble in ether and in alcohol, but insoluble in water.

Crude digitalacrin likewise contains a resin or fat precipitable by basic acetate of lead. By decomposing the lead-precipitate under alcohol with sulphydric acid, and leaving the filtrate to evaporate, the resin called digitalin-fat or digitaloin is obtained, in white crystalline scales, which melt to an oil at a gentle heat, and are said to consist of  $C^{23}H^{24}O^6$ . Walz regards the compound as a glyceride, but does not state whether glycerin can be obtained from it.

**DIGITALEIN.** *Digitaline.* A substance said by Kossmann (Buchn. Repert. xcii. 348) to be contained in the precipitate thrown down by basic acetate of lead from the aqueous extract of foxglove (*Digitalis purpurea*). The precipitate is first exhausted with ether, which dissolves digitoleic acid, the residue is boiled with alcohol, and the solution evaporated: it then deposits the digitalein in the crystalline form. This body is slightly soluble in water, easily in alcohol, insoluble in ether. The aqueous solution is precipitated by lead-salts, but not by ferrous sulphate or silver-salts.

**DIGITALETIN.** Walz's name for pure digitalin.

**DIGITALIC ACID.** (P. Morin, J. Pharm. [3] vii. 294).—An acid contained in foxglove (*Digitalis purpurea*). To obtain it, an aqueous infusion of the leaves is evaporated to the consistence of an extract, and gradually mixed with alcohol of 92 or 94 per cent. as long as anything separates from it. The mixture is left to clarify, and the alcohol is decanted and distilled in the water-bath, till the residue acquires the consistence of a thick extract. This residue is boiled several times with ether, which dissolves digitalic acid and digitalin, and the ethereal solution is shaken up with baryta till it acquires an alkaline reaction, whereby the digitalic acid is precipitated as a barium-salt, while the digitalin remains in solution. This salt is washed with ether and strong alcohol to remove digitalin, and then decomposed by dilute sulphuric acid, care being taken not to convert all the baryta into sulphate. The filtered liquid is concentrated by evaporation out of contact of air, then mixed with strong alcohol to separate the undecomposed barium-salt, and the alcoholic filtrate is evaporated in vacuo. Throughout the whole process, great care must be taken to prevent access of air to the material.

Digitalic acid crystallises in needles. It has a peculiar odour, which becomes strong when the acid is heated, and a decided acid taste; it reddens litmus. It is not volatile, but melts easily, becoming coloured and charred at a higher temperature, without evolution of ammonia. It is very soluble in water, but the solution soon becomes coloured, the change being accelerated by light and heat. It is moderately soluble in alcohol, and the solution keeps better; less soluble in ether. It has not been analysed.

It expels carbonic acid from alkaline carbonates, but its salts are decomposed by contact with the air, even more easily than the free acid. The digitalates of potassium, sodium, barium, calcium, strontium, magnesium, zinc, and ferricum are soluble in water; the copper-salt, the ferrous salt, and the lead and silver-salts are obtained by precipitation.

The name digitalic acid is also applied by Kossmann to a product,  $C^{24}H^{20}O^{23}$ , obtained by boiling digitalin with moderately dilute soda-ley or with lime. It is precipitated by acids from the alkaline solution in white flocks, may be crystallised from alcohol, and forms crystalline salts with bases. By boiling with acids it is resolved into digitaliretin and glucose.

**DIGITALICRIN.** See DIGITALACRIN.

**DIGITALIN.** (Le Royer, Bibl. Univ. xxvi. 102.—Lancelot, Ann. Ch. Pharm. xii. 251.—Trommsdorff, *ibid.* xxiv. 240; and Arch. Pharm. x. 113.—Homolle, J. Pharm. [3] vii. 57.—O. Henry, *ibid.* vii. 460.—Homolle and Quevenne, *Mémoires sur la Digitaline*, Paris, 1851; abstr. Repert. Pharm. [3] ix. 2.—Walz, Jahrb. pr. Pharm. xiv. 20; xxi. 29; xxiv. 86; Gerh. Traité, iv. 286.—N. Jahrb. Pharm. viii. 332; ix. 302; x. 319; Jahresber. d. Chem. 1847, p. 646; 1851, p. 567; 1852, p. 679;

1853, p. 568; 1857, p. 520; 1858, p. 528. — Delffs, N. Jahrb. Pharm. ix. 26; Jahresber. d. Chem. 1858, p. 528. — Kossmann, J. Pharm. [3] xxxviii. 5.) — The active principle of *Digitalis purpurea*. It is obtained by exhausting the comminuted leaves of foxglove with alcohol; concentrating the extract by evaporation; treating the syrupy residue with acetic acid; decolorising with animal charcoal; treating the resulting solution, which contains acetate of digitalin, with tannin, whereby the digitalin is precipitated as tannate; and decomposing this precipitate with oxide of lead, which sets the digitalin free. It is then decolorised with animal charcoal and crystallised from ether.

On the large scale, digitalin may be directly precipitated from the aqueous decoction of the plant by tannin.

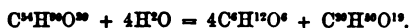
According to Delffs and Walz, digitalin prepared as above is not pure. Delffs purifies it from an admixed resinous body by washing it with cold alcohol of 70 per cent., and dissolving the residue in boiling alcohol of 85°, from which the pure digitalin separates on cooling. Walz treats the impure digitalin with ether, which extracts digitalacrin, and the residue with water, which dissolves digitasolin and leaves pure digitalin. (Walz's *Digitalin*.)

Digitalin is white, difficult to crystallise, inodorous, has a bitter taste, is very sparingly soluble in water, to the extent of only  $\frac{1}{1000}$  at the boiling heat, moderately soluble in ether, freely in alcohol; according to Delffs, only when it is contaminated with resin. Digitalin exerts a powerful action on the animal economy, even a small dose of it producing poisonous effects. The smallest quantity of it introduced in the state of powder into the olfactory organs produces violent sneezing.

The composition of digitalin has not been determined with certainty; according to Delffs, it is  $C^{22}H^{30}O^8$ ; according to Kossmann,  $C^{24}H^{32}O^{10}$ , or  $C^{24}H^{30}O^{10}$ .

Digitalin becomes coloured at 180° C., and decomposes with much tumefaction when heated above 200°. Sulphuric acid dissolves it, acquiring thereby a brown colour, which soon changes towards crimson. The solution poured into water colours it greenish. Hydrochloric acid dissolves digitalin, forming a yellow liquid, which gradually changes to a dark green. Tannin precipitates digitalin from its aqueous solution. It is not precipitated by nitrate of silver, mercurous nitrate, acetate of copper, or acetate of lead, either neutral or basic.

According to Ludwig and Delffs, digitalin boiled with mineral acids yields a liquid which reduces an alkaline cupric solution. According to Kossmann, digitalin ( $C^{24}H^{30}O^{10}$ ) boiled with dilute sulphuric acid yields glucose and digitaliretin,  $C^{22}H^{30}O^8$ .



According to Walz, pure digitalin, called by him *digitaletin* ( $C^{22}H^{30}O^8$ ), is resolved by boiling with dilute sulphuric acid, partly with abstraction of 2 at. water, into paradigitaletin ( $C^{22}H^{30}O^7$ ), partly into digitaliretin ( $C^{16}H^{20}O^8$ ) and glucose:



Digitalin boiled with moderately dilute soda-ley, or with lime, takes up water, and is converted into Kossmann's digitalic acid (p. 328).

**DIGITALIN-FAT.** See DIGITALACRIN.

**DIGITALIRETIN.** A product of the decomposition of digitalin by dilute sulphuric acid. Its formulae, as determined by Kossmann and by Walz, have just been given. According to Kossmann, it is sparingly soluble in ether, easily in alcohol, and crystallises from hot alcohol in shining grains.

**DIGITALIS.** A genus of plants belonging to the natural order *Scrophulariaceae*. The best known species is the common foxglove, *Digitalis purpurea*, the herb of which is used in medicine, both as a diuretic and for its retarding effect on the circulation. From the results of numerous chemical investigations, this plant has been found to contain the following more or less problematical compounds, besides the ordinary vegetable constituents, starch, sugar, albumin, oil, &c.: — *Digitalin*, already described. *Picrin*, obtained by agitating the aqueous extract of the plant with ether. *Scaptin*, an acrid extractive substance, not separated from the aqueous extract by ether (Radig). Morin found, besides digitalin, a volatile acid, *antirrhinic acid* (i. 348), and a non-volatile acid, *digitalic acid* (p. 328). Walz has obtained, as volatile principles, *digitalosmin* and *digitalissic acid* (valeric acid); and as non-volatile principles, *digitalin*, *digitasolin*, *digitalacrin*, *digitaloin*, and *digitaloic acid*. Whether all these bodies are really distinct, or whether they have been obtained quite pure, is a



point not yet quite decided; but Walz's analyses certainly agree very well with his formulae.

According to Buchner (Repert. [3] ix. 38), the seeds of foxglove contain about 3 per cent. of digitalin, more indeed than the herb, and 40 per cent. of their weight of a drying oil, which is said to hold the digitalin in combination. The seed-capsules and calices contain but a small quantity of digitalin, about 0.3 per cent.

From *Digitalis lutea*, Walz obtained, by distillation, digitalosmin, and a peculiar volatile fatty acid, isomeric with valeric acid; also formic acid, acetic acid, digitalin, digitalacrin, and digitasolin. (Hand. d. Chem. 2<sup>o</sup> Aufl. ii. [3] 465.)

**DIGITALISSIC ACID.** See DIGITALIS.

**DIGITALOSMIN.** The odoriferous principle of *Digitalis purpurea* and *D. lutea*, obtained as a fatty film by distilling either of these plants with water. It is a camphoroidal substance insoluble in cold water, soluble in alcohol and in ether, melts when heated with water, and is not dissolved by ammonia. (Walz.)

**DIGITASOLIN.** (Walz, N. Jahrb. Pharm. ix. 302; Jahresber. d. Chem. 1858, p. 529.)—This substance, now called by Walz, *digitalin*, constitutes, according to his observations, the principal portion and the active principle of commercial digitalin. Its formula, according to Walz's latest determination, is  $C^{22}H^{40}O^{14}$ . When commercial digitalin is exhausted with ether (to remove digitalacrin), the dry residue treated with water, and the aqueous extract either purified with animal charcoal and evaporated, or treated with oxide and basic acetate of lead, then freed from lead by sulphuric acid, neutralised with ammonia, and precipitated by tannin, digitasolin is obtained as a yellowish amorphous mass, which is soluble in 120 pts. of cold and 40 pts. of boiling water, differing therein essentially from the compound usually called digitalin. (Walz's *Digitalin*, p. 328.)

Digitasolin is decomposed by boiling with dilute sulphuric acid, yielding digitaliretin,  $C^{16}H^{28}O^3$ , soluble in alcohol and ether, and melting at  $60^{\circ}C$ , and paradigitalin,  $C^{22}H^{40}O^7$ , insoluble in ether, soluble in alcohol, and remaining solid at  $100^{\circ}C$ . (p. 328.)

**DIGITOLEIC ACID.** (Kossmann, J. Chim. méd. [3] ii. 377.)—A kind of fatty acid contained in the leaves of *Digitalis purpurea*. It is obtained by exhausting the leaves with cold water, precipitating with acetate of lead, decomposing the precipitate with carbonate of sodium, treating the filtered solution with hydrochloric acid, which precipitates the digitoleic acid, and crystallising the product from strong alcohol. The acid crystallises in slender needles grouped in stars or grains and having a green colour. Taste bitter, odour agreeably aromatic. Sparingly soluble in water, very soluble in alcohol and ether. Reddens litmus and expels carbonic acid from alkaline and earthy carbonates.

The *digitoleates* are yellow or greenish yellow; those of the alkalis are soluble; the rest insoluble. The solutions of the alkaline salts froth like soap-water.

**DIHYDRITE.**  $Cu^2PO_4 \cdot 2CuHO$ .—A basic phosphate of copper from Nischne-Tagilsk in the Ural. (See PHOSPHATES.)

**DIKA-BREAD.** A vegetable substance somewhat resembling cocoa, prepared from the fruit of the *Mangifera Gabonensis*, a tree growing abundantly on the west coast of Africa, from Sierra Leone to the Gaboon. The fruit, which is about as large as a swan's egg, contains a white almond having an agreeable taste. These almonds, when coarsely bruised and warm-pressed, form dika-bread, which has a grey colour, with white spots, smells like roasted cocoa and roasted flour, has an agreeable, somewhat bitter and astringent taste, and is greasy to the touch. It is a valuable article of food, and is used abundantly by the natives of the country.

Dika-bread contains a large quantity of fat. O'Rorke (J. Pharm. [3], xxxi. 275) obtained from it from 79 to 80 per cent. solid fat, melting at  $30^{\circ}C$ . Oudemans (J. pr. Chem. lxxxi. 356) obtained by exhaustion with ether, 66 per cent. fat, melting at  $33^{\circ}C$ . The fat has an agreeable odour, and is easily saponified by potash, yielding myristic and lauric acids, but no volatile acid.

**DILATATION.** See HEAT.

**DILATOMETER.** This name is given by Kopp to a thermometric apparatus for measuring the expansion of liquids (see HEAT); by Silbermann to an instrument which he uses for measuring the expansion of a mixture of two liquids, and thence determining their relative quantities; e.g. for determining the strength of aqueous alcohol.

**DILITURIC ACID.** *Nitrodilitic acid*. (Schlieper, Ann. Ch. Pharm. lvi. 23.)



When aqueous alloxantin is boiled with hydrochloric acid; the mixture of allitric acid and alloxantin which separates on cooling, treated with nitric acid, to dissolve out the latter; the nitric acid solution treated with sulphuretted hydrogen, and filtered; and the filtrate mixed with nitric acid, and evaporated to one-third;—a yellowish powder is obtained, which, by recrystallisation from hot water yields yellow laminae. Schlieper assigns to this compound the formula  $C^4H^4N^4O^4$ , and regards it as the ammonium-salt of a peculiar acid, which he has not succeeded in isolating, which he calls Dilituric acid. The compound is nearly insoluble in cold, sparingly soluble in hot water; insoluble in ammonia; soluble in sulphuric acid, and reprecipitated unchanged by water; neither dissolved nor decomposed by nitric acid. It is soluble in dilute potash, with evolution of ammonia: from the solution acids precipitate acid dialurate of potassium. The acid appears to be dibasic. Besides the potassium-salt, Schlieper has analysed its silver-salt. F. T. C.

**DILLNITE.**  $4Al^4O^3 \cdot 3SiO^2 + 8H^2O$ . (Haidinger, Pogg. Ann. xxviii. 575.—Jahresber. d. Chem. 1849, 259.)—The compact argillaceous mass in which the diasporé of Schemnitz is imbedded, consists of three varieties, one of which (a) is agalmatolite, while the other two (b and c) contain a mineral not previously observed, to which Haidinger gives the name of *Dillnite*, from the locality, Dillna, near Schemnitz, where it occurs. The agalmatolite (a) is translucent, with grey or greenish colour, fatty lustre and splintery fracture. Hardness = 2.5 to 3; specific gravity = 2.735. Dillnite (b), called *collyrite* at Schemnitz, has the composition above stated: it is white, opaque and dull, earthy, and adheres strongly to the tongue. Hardness, 1.8 to 2. Specific gravity 2.574. The variety c, called *Bildstein* at Schemnitz, is also white, opaque and dull, but has a flat conchoidal or uneven fracture; hardness 3.5 and specific gravity 2.835: it is dillnite mixed with a hydrate of aluminium,  $Al^4H^4O^4$  or  $Al^4O^2 \cdot 4H^2O$ . The following are the analyses of these minerals:

	SiO <sup>2</sup>	Al <sup>4</sup> O <sup>3</sup>	Ca <sup>2</sup> O	Mg <sup>2</sup> O	Fe <sup>2</sup> O	K <sup>2</sup> O and Na <sup>2</sup> O	H <sup>2</sup> O	Total.
a.	49.5	27.5	5.6	0.7	1.0	10.2	5.1	= 99.0
b.	23.5	53.0	0.9	1.8	trace	trace	20.05	= 99.25
c.	22.4	56.4	trace	0.4	. .	. .	21.1	= 100.4

The diasporé is found most abundantly in the second variety.

**DILL, OIL OF.** *Oil of Celery, Oleum anethi.* The volatile oil of *Apium* (or *Anethum graveolens*). It has a pale yellow colour, becoming brownish by age, the same pungent odour as the seeds, and a sweetish taste. Specific gravity 0.88 to 0.91; of old oil, according to Zeller, 0.95. Sparingly soluble in water, easily in alcohol and ether. Boils at about 190° C. (Handw. d. Chem. 2<sup>te</sup> Aufl. ii. [3] 468.)

**DIMAGNETITE.** A mineral consisting mainly of ferroso-ferric oxide, which occurs in rhombic prisms at Monroe, Orange County, New York, and is regarded by Shepard (Sill. Am. J. [2] xiii. 392) as a distinct species. According to Dana, however (*Mineralogy*, ii. 206), it is a pseudomorph of magnetite after lievrite.

**DIMETAPHOSPHORIC ACID.** See PHOSPHORUS, OXYGEN-ACIDS OF.

**DIMORPHINE.** A sulphide of arsenic from the Solfatara, Pozzuoli. It forms minute trimetric crystals of very complicated form, and is regarded by Scacchi (*M.-m. geol. sulla Campania*, Napoli, 1849) as a distinct species. It has not, however, been analysed, and is perhaps a mere variety of orpiment, which it very much resembles.

**DIMORPHISM, and TRIMORPHISM.** Many substances, both simple and compound, crystallise in forms which belong to two or three different systems of crystallisation, or which, even if they belong to the same system, yet exhibit such difference in their corresponding angles as to render it quite impossible to reduce them to the same form: this was first shown by Mitscherlich in 1823 (Ann. Ch. Phys. [2] xxiv. 264). Such bodies are said to be dimorphous and trimorphous. The difference of crystalline form which they exhibit is associated with difference of specific gravity, hardness, colour, and other properties. Whether a body shall crystallise in one system or another seems to depend chiefly on temperature. Crystals formed at one particular temperature, and then exposed to that temperature at which crystals of a different kind are produced, often lose their transparency, and, without alteration of external form, become changed into an aggregate of small crystals of the latter kind: examples of this alteration of structure are afforded by sulphur, carbonate of calcium, mercuric iodide, and many other bodies. Sometimes the form of the crystal varies according to the solvent from which it separates; thus, arsenious anhydride crystallises from water or hydrochloric acid in regular octahedrons, from alkaline solutions in trimetric prisms.

The most important cases of dimorphism hitherto observed, are as follows:

1. In *elementary bodies*.

*Carbon*, in the diamond, forms crystals belonging to the monometric system; in graphite, to the hexagonal system. If the amorphous varieties, charcoal, anthracite, &c., are likewise taken into account, carbon may be regarded as trimorphous.

*Arsenic, antimony, phosphorus, bismuth, palladium, iridium, copper*, and probably *iron*, likewise crystallise in the monometric and hexagonal systems.

*Tin* exhibits forms belonging to the monometric and dimetric systems.

*Sulphur* crystallises on cooling from a state of solution in sulphide of carbon in rhombic octahedrons belonging to the trimetric system, exactly like those of native sulphur; if, on the other hand, melted sulphur be allowed to cool slowly till a portion of it has become solid, and the still liquid portion be then poured out, the solidified portion exhibits oblique rhombic prisms belonging to the monoclinic system. These are at first perfectly transparent, of a deep yellow colour, and somewhat harder and denser than those of sulphur crystallised in the cold; but after being kept for a few days at ordinary temperatures, they become opaque, and of a straw-yellow colour.

According to Frankenheim (J. pr. Chem. xvi. 5), sulphur assumes the form of the oblique rhombic prism when precipitated from solutions, or sublimed, at temperatures near its melting point.

2. In *compound bodies*. A compound is said to be dimorphous, only when the two forms which it assumes are perfectly identical in chemical composition. Thus, a salt which crystallises in two forms is not dimorphous, if these forms belong to different hydrates; thus the two hydrates of sulphate of nickel, viz.  $\text{Ni}^2\text{SO}^4 + 6 \text{ aq.}$ , which is dimetric, and  $\text{Ni}^2\text{SO}^4 + \text{aq.}$ , which is trimetric, do not afford an instance of dimorphism.

*Cuprous oxide* occurs in ordinary red copper ore in regular octahedrons and other forms belonging to the monometric system, but in copper-bloom it exhibits forms of the trimetric system.

*Protoxide of lead* crystallises after fusion, as well as from a saturated solution in hot concentrated caustic potash, in yellow rhombic octahedrons. If, however, the solution is not fully saturated with oxide of lead, so that crystallisation does not take place till after complete cooling, red crystalline scales are deposited on the yellow rhombic octahedrons just formed: if the red crystals are heated, they turn yellow on cooling, in consequence of passing into the first form. (Mitscherlich, J. pr. Chem. xix. 461.)

*Titanic oxide*,  $\text{TiO}^2$ , occurs in nature in the three forms of anatase, rutile, and brookite. Anatase and rutile are both dimetric, but their angles are incompatible, so that they cannot be reduced to the same primitive form; moreover, the specific gravity of anatase is 3.826, that of rutile 4.249. Brookite is trimetric.

*Arsenious oxide*,  $\text{As}^2\text{O}^3$ , generally crystallises in regular octahedrons; but Wöhler (Pogg. Ann. xxvi. 177) found it also in the form of native oxide of antimony,  $\text{Sb}^2\text{O}^3$  (valentinite), which belongs to the trimetric system. Wöhler also obtained artificially crystallised oxide of antimony in regular octahedrons. Consequently  $\text{As}^2\text{O}^3$  and  $\text{Sb}^2\text{O}^3$  are *iso-dimorphous*; i. e. they are capable of crystallising in two different forms which are similar each to each.

*Cuprous sulphide*,  $\text{Cu}^2\text{S}$ , appears in copper-glance in crystals of the trimetric system; but Mitscherlich (Pogg. Ann. xxviii. 167), by melting together large quantities of copper and sulphur, obtained it in regular octahedrons. These two forms are similar to those of the red oxide of copper.

*Disulphide of iron* occurs in nature as iron pyrites in crystals belonging to the regular system, and as marcasite, in forms of the trimetric system, the latter being of a paler yellow and much softer.

*Mercuric iodide* separates from solution, and likewise sublimes at a very gentle heat, in scarlet tables belonging to the dimetric system, but when sublimed at a higher temperature, in sulphur-yellow rhombic tables of the monoclinic system. The red crystals turn yellow when heated, and resume their red tint on cooling. The yellow crystals obtained by sublimation retain their colour when cooled; but on the slightest rubbing or stirring with a pointed instrument, the part which is touched turns scarlet, and this change of colour extends, with a slight motion, as if the mass were alive, throughout the whole group of crystals as far as they adhere together.

*Carbonate of calcium*,  $\text{Ca}^2\text{CO}^3$ , in the form of calc spar, whose specific gravity = 2.721, belongs to the rhombohedral; in arragonite, whose specific gravity is 2.931, to the trimetric system. An explanation of this difference was formerly sought in the fact discovered by Stromeyer, viz., that arragonite usually contains small quantities of carbonate of strontium. The same peculiarity is presented by *carbonate of iron* (i. 359), which in sparry iron ore (of 3.872 specific gravity) has the form of calc spar, in junkerite (of 3.815 specific gravity) that of arragonite. Hence  $\text{Ca}^2\text{CO}^3$  and  $\text{Fe}^2\text{CO}^3$  are isodimorphous. If a solution of carbonate of calcium in water containing carbonic acid be left

to evaporate at the ordinary temperature, nothing is obtained but calcespar, in microscopical and, for the most part, truncated primitive rhombohedrons; if, on the contrary, the solution be evaporated over the water-bath, arragonite is obtained in small six-sided prisms, mixed with a few crystals of calcespar, because the temperature of the solution is lower at first than it afterwards becomes, and the specific gravity of the liquid is not higher than 2.808. When an aqueous solution of chloride of calcium is mixed at ordinary temperatures with an aqueous solution of carbonate of ammonium, a voluminous flocculent precipitate of chalky (amorphous?) carbonate of calcium is first produced, which, if immediately collected on a filter, washed and dried, remains unaltered, possessing a specific gravity of 2.716, and appearing under the microscope to consist of small opaque granules; but if this same precipitate be left for some time in the saline liquid from which it has been precipitated, it collects into microscopical crystals of calcespar, of specific gravity 2.719. If the same saline solutions be mixed boiling, the carbonate of ammonium being added to the chloride of calcium, arragonite is obtained, mixed with a small portion of calcespar. If, on the contrary, the chloride of calcium be added to the carbonate of ammonium, arragonite is obtained alone, in exceedingly small crystals of specific gravity 2.949. If, however, these crystals are not immediately collected on a filter, washed, and dried, but allowed to remain in the liquid, they gradually change after the liquid has cooled, and in about a week are completely converted into calcespar; in pure water this transformation goes on much more slowly. When carbonate of calcium is fused under strong pressure, it invariably crystallises on cooling in the form of calcespar. A tolerably large crystal of arragonite falls to pieces at a low red heat without losing weight, and forms a white, opaque, coarse powder, having a specific gravity of only 2.706. Hence it follows that carbonate of calcium crystallises at about 100° C. in the form of arragonite, but at a lower temperature, or at a red heat, in the form of calcespar. The arragonite which occurs in the caverns of volcanic districts must have been formed by infiltration while the mass was yet warm. (H. Rose, Pogg. Ann. xlvii. 353.)

*Nitrate of potassium* usually crystallises in prisms of the form of arragonite: but if a drop of the aqueous solution of this salt be left to evaporate on a glass plate and the crystallisation observed under the microscope, it will be found that, side by side with the prismatic crystals at the edges of the drop, a number of obtuse rhombohedrons of the calcespar form are produced, just like those in which nitrate of sodium crystallises. As the two kinds of crystals increase in size and approach one another, the rhombohedrons become rounded off and dissolve, because they are more easily soluble than the others, while the arragonite-shaped prisms go on increasing in size. When the two kinds of crystals come into immediate contact, the rhombohedral ones instantly become turbid, acquire an uneven surface, and after a short time throw out prisms from all parts of their surfaces. Contact with foreign bodies also brings about the transformation of the rhombohedrons while they are wet. If the drops are so shallow that the liquid dries round the rhombohedrons before they are disturbed, they will remain for weeks without disintegrating, and bear gentle pressure with foreign bodies without alteration; but stronger pressure, or scratching, or the mere contact of a prismatic crystal of saltpetre, causes them to change, a delicate film proceeding, as it were, from the point of contact and spreading itself over their surfaces; they then behave towards foreign bodies like a heap of fine dust, but retain their transparency. The rhombohedrons are also transformed, without alteration of external appearance, when heated considerably above 100° C.: they then become much harder, because the fine powder first produced bakes together into prismatic crystals. A hot solution of saltpetre yields, when slightly cooled, nothing but prismatic crystals; but at 10° C. prismatic and rhombohedral crystals appear together; if alcohol be added, the latter are formed most abundantly; the addition of potash, nitric acid, or nitrate of sodium, produces no alteration. (Frankenheim, Pogg. Ann. xl. 447; also J. pr. Chem. xvi. 1.)

*Sal-ammoniac*, which commonly crystallises in regular octahedrons, appears at higher temperatures to assume forms belonging to the trimetric system. (Frankenheim, J. pr. Chem. xvi. 3.)

*Iodide of potassium*, which usually crystallises in cubes, likewise forms square prisms, with truncated summits, which cannot be regarded as cubo-octahedrons, because their octahedral faces are not equally inclined to all the adjacent prismatic faces;  $P : oP = 120^\circ$ ;  $P : \infty P =$  about 150. (Kane, Phil. Mag. [3] xvi. 222.)

*Chromate of lead* occurs in red lead spar in the form of monoclinic prisms; but in chromate of lead from the Bannat, the same substance presents forms belonging to the dimetric system, having the same angles as molybdate of lead. (Johnston, Phil. Mag. [3] xii. 387.)

*Sulphate of nickel*,  $NiSO_4 + 7 aq.$ , crystallises (a) below 15° C. in trimetric prisms, (b) between 15° and 20° C. (59° and 68° Fahr.) in acute dimetric octahedrons, and (c) above 30° C. (86° Fahr.) in monoclinic prisms; it is therefore *trimorphous*. The right



rhombic prisms (*a*) when exposed to sunlight for a few days, neither liquefy nor lose their form or water of crystallisation, but when broken are found to be made up of square-based octahedrons, often several lines in length.

The following salts, isomorphous with sulphate of nickel, have hitherto been obtained in only two out of the three forms just mentioned. *Sulphate of zinc*,  $\text{Zn}^2\text{SO}_4 + 7 \text{ aq.}$ , crystallises below  $52^\circ \text{C.}$  in form *a*; below  $52^\circ \text{C.}$ , as observed by Haidinger in less transparent crystals, like *c*; if a crystal *a* be heated in oil or in a glass tube above  $52^\circ \text{C.}$ , it becomes soft at certain points without losing water, excepting any that may be adhering to it mechanically, and from these points bundles of milk-white crystals *c* shoot out towards the inside of the transparent crystal, until the whole is completely transformed. If the crystals obtained above  $52^\circ \text{C.}$  be slowly cooled after drying, they remain tolerably clear; but when cooled quickly before drying, they become opaque, and when broken are often found to consist of an aggregate of crystals *a*, these having been first formed in the adhering mother-liquid, and subsequently extended through the crystals already formed. *Sulphate of magnesium*,  $\text{Mg}^2\text{SO}_4 + 7 \text{ aq.}$ , like sulphate of zinc, yields trimetric prisms *a* below  $52^\circ$ , and monoclinic prisms *c* above  $52^\circ$ ; and the crystals *a* when heated above  $52^\circ$  are immediately converted into an opaque aggregate of crystals *c*, which proceed from the surface of the crystals and meet in the middle. *Selenate of zinc*,  $\text{Zn}^2\text{SeO}_4 + 7 \text{ aq.}$ , crystallises at a lower temperature like *a*, at a higher temperature like *b*, and the crystals *a* undergo an alteration of internal structure when exposed to sunshine. (Mitscherlich, Pogg. Ann. vi. 19, and xii. 144.)

*Acid phosphate of sodium*,  $\text{NaH}_2\text{PO}_4 + \text{aq.}$  crystallises in two series of forms, both of which belong to the trimetric system, but have incompatible angles. (Mitscherlich.)

**DINITE.** A fossil resin found in the lignite of Lunigiana in Tuscany. Cleavage, none. Has the appearance of ice, with a yellow tinge. Inodorous and tasteless. Fragile and easily reduced to powder. Insoluble in water, sparingly soluble in alcohol, very soluble in ether and in sulphide of carbon. The ethereal solution, on standing, deposits large crystals of the resin. It melts with the warmth of the hand. Heated in a close vessel, it distils over without perceptible decomposition.

**DINITRAMMONYL**, and **DIBROMONITRACETONITRILE.** See TRINITRACETONITRILE.

**DINITROETHYLIC** and **DINITROMETHYLIC ACIDS.** See NITROUS ETHERS.

**DIOPSIDE.** A variety of augite  $\text{M}^2\text{SiO}_3$ , containing calcium and magnesium, with little or no iron. The crystals appear rectangular in the basal section from predominance of the faces  $\infty \text{P}\infty$  and  $[\infty \text{P}\infty]$ , and are acuminated at the ends with the faces  $+ \text{P}$ ,  $- \text{P}$ ,  $-2\text{P}$ , and several others, the pyramids being also frequently truncated by  $\infty \text{P}$ . Inclination of  $\infty \text{P}$ :  $\infty \text{P} = 87^\circ 6'$ ;  $+ \text{P}$ :  $+ \text{P}$  in the clinodagonal principal section  $= 131^\circ 29'$ ;  $- \text{P}$ :  $- \text{P} = 120^\circ 39'$ ;  $-2\text{P}$ :  $-2\text{P} = 96^\circ 36'$ . Cleavage distinct parallel to  $\infty \text{P}$ ; less distinct parallel to  $\infty \text{P}\infty$  and  $[\infty \text{P}\infty]$ . The crystals are implanted, or less frequently imbedded, and often distorted into fusiform, scaly, or granular aggregations. The granular variety, if coarse and somewhat friable, is called *white coccolite*. Specific gravity  $= 3.2$  to  $2.3$ . Hardness  $= 5.5$  to  $6.0$ . Colour, generally light green or grey; white, if quite free from iron. Lustre, vitreous on the crystalline faces, nacreous on the cleavage faces. Transparent or translucent in various degrees, sometimes on the edges only; the more transparent sorts are sometimes cut for gems. Before the blowpipe, diopside melts to a whitish or grey glass. It is insoluble in acids.

*Analyses.*—*a.* From Tammare, Finland (Bonsdorff, Schw. J. xxxi. 158).—*b.* From Brazil (Kussin, *Rammelsberg's Mineralchemie*, p. 452).—*c.* From the Zillerthal (Wackenroder, Kastn. Arch. xiii. 84).—*d.* From Reichenstein, in Silesia; partly asbestiform (R. Richter, Pogg. Ann. lxxxiv. 383).—*e.* From Pargas in Finland; large grey-green crystals (Arppe, *Anal. af. Finsk. min.* p. 22).—*f, g.* From Schwarzenstein in the Tyrol (T. S. Hunt, Phil. Mag. [4] vii. 501).—*h.* From the Saassgrat between the Rimplschhorn and the Strahlhorn; white, translucent. (Brunner, Jahrb. Min. 1855, p. 186.)

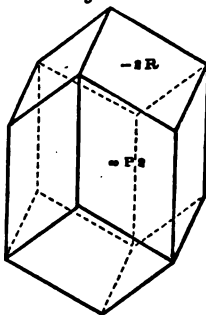
	$\text{SiO}_2$	$\text{CaO}$	$\text{MgO}$	$\text{FeO}$	$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{MnO}$	Loss by ignition.	
<i>a.</i>	54.83	24.76	18.55	0.99	. .	0.28	. .	0.32	= 99.73
<i>b.</i>	55.61	25.11	17.82	1.20	. .	. .	. .	. .	= 99.74
<i>c.</i>	54.16	24.74	18.22	2.50	. .	0.20	0.18	. .	= 100.00
<i>d.</i>	54.50	21.41	18.96	3.00	. .	1.10	. .	1.19	= 100.16
<i>e.</i>	52.67	21.03	19.52	4.54	. .	0.54	. .	. .	= 98.30
<i>f.</i>	51.60	23.80	17.69	. .	0.35	6.15	. .	1.10	= 100.59
<i>g.</i>	50.90	23.74	18.14	. .	. .	6.77	. .	0.90	= 100.45
<i>h.</i>	56.13	25.78	16.92	. .	2.02	. .	trace	. .	= 100.85

A transparent colourless variety of diopside called *alalite*, found at Ala in Piedmont, is cut for gems. *Massite* is a variety from Massa in Piedmont of greyish-green colour, with lamellæ parallel to the base, and sometimes contorted. These two varieties contain very little iron.

Diopside has also been found as a furnace-slag (Hausmann, J. pr. Chem. lvi. 186), and is produced artificially by passing vapour of chloride of silicon over a mixture of lime and magnesia at a red heat. (Daubrée, Compt. rend. xxxix. 163.)

**DIOPTASE.** *Emerald Copper, Emerald Malachite, Smaragdochalcite, Achirite,*  $\text{Cu}^*\text{SiO}_3 + \text{H}^2\text{O}$  or  $(\text{Cu}^*\text{H}^*)\text{SiO}_3$ .—This mineral crystallises in rhombohedral combinations derived from a primary form R, for which the length of the principal axis is 0.6295, and the angle R : R in the terminal edges =  $126^\circ 17'$ . Ordinary combination  $-2\text{R} . \infty \text{P}2$  (fig. 369);  $-2\text{R} : -2\text{R}$  in the terminal edges =  $96^\circ 48'$ . Cleavage very distinct parallel to R. It occurs in single crystals and implanted in geodes. Specific gravity = 3.278 – 3.348. Hardness = 5. Colour emerald-green. Streak green. Lustre vitreous. Transparent to sub-translucent. Fracture conchoidal, uneven. Brittle. When heated in a tube, it gives off water and turns black. Infusible before the blowpipe; turns black in the outer, red in the inner flame. Gives with phosphorus-salt a skeleton of silica and the reactions of copper; and with soda a button of copper. Dissolves in hydrochloric acid, with separation of gelatinous silica.

Fig. 369.



*Analyses.*—a, b, Damour (Ann. Ch. Phys. [3] x. 485);—c, d, Hess (Pogg. Ann. xvi. 360).

	$\text{SiO}_2$	$\text{Cu}_2\text{O}$	$\text{H}_2\text{O}$	$\text{Fe}_2\text{O}_3$	$\text{Fe}^*\text{O}_3$	$\text{CaCO}_3$	$\text{Al}_2\text{O}_3$	$\text{CaO}$	$\text{Mg}_2\text{O}$	
a.	38.93	49.51	11.27	.	.	.	.	.	.	= 99.71
b.	36.47	50.10	11.40	.	0.42	0.36	.	.	.	= 98.74
c.	36.85	45.10	11.52	.	.	.	2.36	3.39	0.22	= 99.44
d.	36.60	48.89	12.29	2.00	.	.	.	.	.	= 99.78

Diopside occurs at Altyn Tubé, Berghes-Karkalinsk, and Oni in Siberia, and in the Duchy of Nassau between Oberlahnstein and Braubach.

**DIORITE.** Greenstone, containing soda- instead of potash-felspar. (See GREENSTONE.)

**DIOSCOREA.** A genus of plants of the Smilacæ order, the tubers of which, called *yams*, are very rich in starch, and are much used as food in the West Indies and other tropical countries. In a root of *Dioscorea alata* from the Antilles weighing eleven kilogrammes, Payen (Compt. rend. xxv. 182) found 79.6 per cent. water, and

	In the middle.	At the end of the root.
Non-azotised substance . . . . .	85.0	74.6
Azotised substance . . . . .	9.5	16.4
Mineral constituents . . . . .	5.5	9.0

The tubers of *D. bulbifera* were found to contain 10.5 per cent. starch (Pharm. J. Trans. vi. 23). The tubers of *D. Batatas* (the *Chinese yam*, *Ignams de Chine*), grown in the neighbourhood of Paris, have been analysed by Frémy (Compt. rend. xl. 128); the same from Algeria, by Boussingault and by Payen; the same grown in the Botanic Garden at Bonn by Grouven (Chem. Centralbl. 1867, p. 686). The tubers, after drying over the water-bath, yield by trituration, a powder which may be kneaded with water to a dough, like wheat-flour. The fresh tubers yield in 100 parts:

	Frémy.	Boussin- gault.	Payen.	Grouven.
Starch . . . . .	16.0	13.1	16.7	8.0
Albuminous substance . . . . .	1.5	2.4	2.5	1.1
Fat, sugar, &c. . . . .	1.1	0.2	0.3	6.0
Cellulose . . . . .	1.0	0.4	1.4	0.7
Mineral salts . . . . .	1.1	1.3	1.9	1.1
Water . . . . .	79.3	82.6	77.1	83.0

The albuminous substance does not coagulate till after long continued boiling (Frémy). Suersen (Scheerer's Journ. [1802] viii. 600), found in the tubers of *Dioscorea sativa*, 23 per cent. starch, 68 woody fibre, gum, &c.



**DIOSMA CRENATA.** *Buchu.* The leaves of this plant, a native of the Cape of Good Hope, contain about 0.7 per cent. of volatile oil, 21.2 gum, and 2.15 resin. According to Brandes (*Arch. Pharm.* xxii. 242) they also contain a bitter principle, *diosmin*, which is yellowish-brown, bitter, and soluble in water.

**DIOXYLITE.** Syn. with LANARKITE.

**DIPHANITE.** A variety of margarite, occurring in the emerald mines of the Ural, together with chrysoberyl and phenacite, in hexagonal prisms with perfect basal cleavage. Specific gravity = 3.04 — 3.97. Hardness = 5 — 5.5. Colour, white to bluish. Before the blowpipe it becomes opaque, and fuses with intumescence in the inner flame to a white enamel. With a little soda it forms a blebby glass. Contains, according to Jewreinow's analysis, 34.02 per cent.  $\text{SiO}_2$ , 43.33  $\text{Al}_2\text{O}_3$ , 13.11  $\text{CaO}$ , 3.02  $\text{Fe}_2\text{O}_3$ , 1.05  $\text{Mn}_2\text{O}_3$  and 5.34 water = 99.87, whence approximately the formula  $(\text{M}^2\text{O}.\text{SiO}_2).(2\text{Al}^3\text{O}_3.\text{SiO}_2) + \text{H}_2\text{O}$  or  $\text{M}^2\text{SiO}_4.al^3\text{HO}^2$ . (Nordenskiöld, *Petersb. Acad. Bull.*, v. 17; *Rammelsb. Mineralch.* p. 843.)

**DIPHENIN.**  $\text{C}^6\text{H}^5\text{N}^2$  or  $\text{C}^{12}\text{H}^{12}\text{N}^4$ . (Laurent and Gerhardt, *Compt. chim.* 1849, 417.) Dinitrazobenzene (i. 478) is boiled with alcohol and sulphide of ammonium till most of the alcohol is driven off; the liquid is diluted with water, mixed with a slight excess of hydrochloric acid, filtered hot, and precipitated by ammonia; and the crystalline precipitate is purified, either by recrystallisation from ether, or by converting it into sulphate, which is washed with cold water and alcohol, dissolved in boiling dilute hydrochloric acid, and precipitated by ammonia. Diphenin is a yellow crystalline body, dissolving with red colour, in hydrochloric or nitric acid; the former solution gives with dichloride of platinum a dark carmine precipitate of chloroplatinate,  $\text{PtCl}_2\text{C}^6\text{H}^5\text{N}^2$ . The sulphate is insoluble in water. F. T. C.

**DIPLOBASE.** Syn. with ALSTONITE (i. 149).

**DIPLOITE.** *Latrobeite.* A variety of ANORTHITE (i. 308).

**DIPPEL'S OIL.** *Purified Hart's-horn oil*, or *Animal oil*, *Oleum animale Dippelii*, *Ol. cornu cervi rectificatum*. An oil originally prepared as a medicine by Dippel, an apothecary of the seventeenth century, from crude fetid animal oil (*Ol. cornu cervi fætidum*) by submitting it to repeated rectification *per se*, till it no longer left any black residue. The oil thus obtained is colourless, highly refractive, has a not unpleasant odour, somewhat like that of cinnamon, and a burning taste, with sweetish after-taste, like a mixture of pepper and cinnamon: its specific gravity is 0.865. When kept for some time it turns yellow, especially if exposed to light.

Animal oil is now more generally purified by rectifying it with addition of sand, lime, or water. That which is rectified with water is very mobile, has a very pungent disagreeable odour, a nauseous burning taste, and a specific gravity of about 0.75.

Nearly all the animal oil of commerce is now obtained by the destructive distillation of bones, in fact as a by-product in the preparation of bone-black.

The composition of animal oil varies greatly according to the mode of preparation; but in all cases it consists of a basic and non-basic portion, the former being a mixture of numerous volatile bases, including ammonia and pyrrrol, and the latter consisting mainly of benzene and its homologues. (See BONE-OIL, i. 625.)

**DIPYRE.** *Schmelzstein*, *Leucolithe de Mauléon*. A silicate found with talc and chlorite in an unctuous argillite near Mauléon in the lower Pyrenees, crystallised in four-sided prisms, with rounded ends, apparently dimetric like scapolite, with lateral and diagonal cleavage. Specific gravity = 2.646. Hard enough to scratch glass. Colour whitish or reddish, lustre vitreous. Transparent to translucent; opaque when weathered. Before the blowpipe it becomes opaque and melts with intumescence to a white blebby glass. Melts easily with phosphorus salt, excepting a skeleton of silica. Forms a limpid glass with soda. Attacked with difficulty by the strongest acids, even when pulverised. According to an analysis by Delesse (*Compt. rend.* xviii. 994, 1844), it contains 55.5 per cent.  $\text{SiO}_2$ , 24.8  $\text{Al}_2\text{O}_3$ , 9.0  $\text{CaO}$ , 9.4  $\text{Na}_2\text{O}$ , 0.7  $\text{K}_2\text{O}$ , whence approximately the formula  $4(2\text{M}^2\text{O}.3\text{SiO}_2) + 3(2\text{Al}^3\text{O}_3.3\text{SiO}_2)$ .

**DISACRONE.** See DISACRYL.

**DISACRYL.** (Redtenbacher, *Ann. Ch. Pharm.* xlvii. 114.) Acrolein when kept for some time, even in close vessels, changes, sometimes into a flocculent substance called *disacryl* or *disacrone*, sometimes into a resinous matter, *disacryl resin*.

Disacryl is a white, amorphous, tasteless, inodorous powder, which becomes strongly electrical by friction. It is insoluble in water, acids, alkalis, sulphide of carbon, and oils, either fat or volatile. It dissolves slowly in melted potash, and is precipitated by acids from the solution of the product. It gives by analysis 61.2 per cent. carbon,



and 7.43 hydrogen, whence Redtenbacher deduces the formula  $C^6H^7O^2$  (carbon 60.6, hydrogen 7.1). It is perhaps isomeric with acrolein.

*Disacryl-resin* is a white powder which melts at  $100^\circ C.$ , and forms on cooling a diaphanous brittle mass. It is insoluble in water, but soluble in alcohol and in ether; the alcoholic solution reddens litmus and is precipitated by water. It dissolves in aqueous alkalis and is precipitated by acids. The alcoholic solution precipitates the salts of copper, lead, and other metals. The resin gives by analysis 66.6 C and 7.4 H, whence Redtenbacher deduces the formula  $C^{10}H^{14}O^3$ . (Carbon 66.3, hydrogen 7.2.)

**DISCRASITE.** Syn. with ANTIMONIAL SILVER (i. 317).

**DISOMOSE.** Syn. with NICKEL-GLANCE.

**DISTERRITE.** See CLINTONITE (i. 1026).

**DISTHEWE.** See KYANITE.

**DISINFECTANTS.** See *Ure's Dictionary of Arts, Manufactures, and Mines* (ii. 27).

**DISTILLATION** is the conversion of a substance into vapour, and the condensation of the vapour in another part of the apparatus by cooling, the object of the operation being generally to separate an easily vaporised body from one which is less volatile. It is called especially *distillation*, when the vapour condenses into a liquid, and *sublimation* when it condenses into a solid. In either case the body to be vaporised is enclosed in an alembic flask, retort, or still, and the vapour is conducted through a tube or series of tubes kept cool into a *receiver*. In distillation on the large scale, the conducting tube is in the form of a worm enclosed in a tub, through which cold water is constantly flowing. For laboratory experiments, sufficient cooling power may sometimes be obtained by simply immersing the receiver in cold water, or by directing a stream of cold water on the neck of the retort, surrounded for the purpose with bibulous paper. To obtain greater cooling power, Liebig's condenser is used, which consists of a glass tube enclosed within a metal cylinder, through which cold water is continually flowing in a direction contrary to that of the vapour. For details and figures of apparatus, see *Ure's Dictionary of Arts, Manufactures, and Mines* (ii. 36).

**DISTILLATION, DRY or DESTRUCTIVE.** These terms are applied to the decomposition which organic substances undergo when heated out of contact with the air, or at all events, in such a manner that the constituents of the air take no part in the reaction. Some organic compounds boil at so low a temperature that, when heated in a retort, they pass over unchanged, especially if the air be excluded; *e. g.*, alcohol, ether, volatile oils; others, on the contrary, which would not boil till raised to a higher degree of heat, undergo decomposition before they attain the boiling temperature.

Compounds whose boiling points are not much above the temperatures at which their decomposition begins, pass over to a certain extent undecomposed; because the vapours and gases produced by the decomposition of the one part, take up the other part of the compound below the boiling temperature in the form of vapour, just as water evaporates in the air considerably below its boiling point. Thus, oxalic acid, margaric acid, and other fatty acids, also pinic acid, and certain other resins, indigo-blue, &c., undergo but partial decomposition. Such compounds may therefore be volatilised without decomposition, if they are heated in open vessels to a temperature somewhat below that at which they decompose; or in a wide distillatory apparatus filled with air: or in a tube or a conical enlargement of it, through which is passed a stream of air—or if the air exerts an oxidising action—of hydrogen, nitrogen, or carbonic acid gas; also when carefully heated in *vacuo*.

A contrary action is exerted by sand, brickdust, &c., mixed in large quantities with the organic compound, even if the boiling point of that compound be below the temperature at which it decomposes: for the bubbles of vapour are mechanically retained by the pulverulent mixture, and raised by the heat which penetrates the containing vessel, to the degree at which their decomposition takes place. Alcohol is partially decomposed by this treatment, and benzoic acid almost completely.

The apparatus used for destructive distillation consists of retorts of glass, earthenware, or metal, according to the temperature required, filled with good-sized exit-tubes, and communicating with well-cooled receivers of considerable capacity. For operating on small quantities of substances, Greville Williams, who has worked extensively on the subject, uses a small still made from a glue-pot, and having a copper head fitted to it. The luting for all temperatures not exceeding  $700^\circ F.$  may be a mixture of  $\frac{1}{2}$  linseed and  $\frac{1}{2}$  almond meal, made into a mass of the consistence of putty. For quantities of material not exceeding 15 or 20 lbs., a stout semi-cylindrical cast-iron pot may be used, having a broad flange round the edge and a cover fitting it like a saucepan-lid.

For operations on the manufacturing scale, large retorts of cast iron or fire-clay are employed, as in gas-works. (See *Ure's Dictionary of Arts, Manufactures, and Mines*, ii. 44.)

Volatile organic compounds are decomposed by passing them through a red-hot tube, usually filled with fragments of glass or pumice, to increase the heating surface.

The causes of decomposition by heat are as follows:—The affinity of the oxygen for the hydrogen and the carbon, tending to form water, carbonic oxide and carbonic anhydride, is greater than that by which the elements in the organic compound are held together. These strong affinities are brought into action by heat. Hence those compounds which contain most oxygen decompose at much lower temperatures than those which contain little or none. To this rule, however, there are many exceptions; Acetic acid,  $C^2H^4O^2$ , is a body rich in oxygen; but its vapour is but little altered in composition by passing through a tube at a low red heat; acetate and cyanate of potassium also, are not decomposed when heated to low redness out of contact with air.

In compounds containing nitrogen, the affinity of that element for hydrogen likewise assists the decomposition. The ammonia which is then abundantly formed, does not, however, pass over in the free state, but in combination with an acid, as with carbonic, acetic acid, &c.

If the compound contains chlorine, bromine, iodine, or sulphur, these elements, if they do not separate in the free state, or enter into volatile organic compounds, are given off in combination with hydrogen, in the form of hydrochloric, hydrobromic, hydriodic, or sulphuric acid. Part of the sulphur and chlorine may also be evolved in the form of sulphide or chloride of carbon.

At high temperatures, moreover, decomposition is facilitated by the great tendency of certain elements to assume the gaseous form; hence part of the hydrogen and nitrogen are given off in the state of gas, the quantity thus evolved increasing with the temperature; for even the hydrocarbons formed at a moderate heat may be resolved at higher temperatures into hydrogen gas and sooty carbon. The heat may also induce a disposition to the formation of volatile organic compounds, which, when once produced, pass over, and are thus withdrawn from the decomposing action of a stronger heat.

By the formation of the inorganic compounds above mentioned, and by the escape of hydrogen and nitrogen gas, the organic compound (unless it be one of the more highly oxygenised acids, such as oxalic or formic acid) loses oxygen in the greatest relative quantity, hydrogen and nitrogen in smaller quantity, while the residue becomes continually richer in carbon.

Hence those volatile organic compounds which are richest in oxygen, such as acids and alcoholic liquids, pass over principally at the beginning of the distillation. Among acids, the most frequent is acetic acid. It is formed in especial abundance in the distillation of compounds, such as sugar, gum, or wood, which contain oxygen and hydrogen in about the proportion to form water, so that it only requires the addition of a certain number of carbon-atoms to form acetic acid,  $C^2H^4O^2$ , which, being volatile, is withdrawn from the further decomposing action of the heat. Many organic compounds yield other acids, which in some cases are quite peculiar to them (*vid. inf.*). The alcoholic liquids produced in the dry distillation of a few organic compounds are, wood-spirit, lignone, aldehyde, and acetone.

But as the distillation proceeds, compounds containing little or no oxygen appear in continually greater abundance, viz.: 1. *Gaseous hydrocarbons*, such as marsh-gas,  $CH^4$ , olefiant gas or ethylene,  $C^2H^4$ , and tetrylene,  $C^4H^2$ . The last two hydrocarbons are evolved chiefly from compounds containing but little oxygen, such as fats and resins; the greater their proportion in the gaseous mixture, the more brilliant is its flame and the better is it adapted for illumination.—2. *Volatile oils* generally having an offensive odour, and designated, from their mode of formation, *empyreumatic oils*. They are sometimes pure, sometimes slightly oxidised hydrocarbons. To this class of products belong the two empyreumatic oils which Faraday obtained from fat; also eupione, creosote, picamar, and capnomor, obtained by Reichenbach; pyrrol, by Runge, and several oils obtained from resins by Frémy, Couerbe, Laurent, and others; &c. &c.—3. *Camphoroidal compounds*, which may be called *empyreumatic camphors* or *stearoptenes*; they consist wholly of carbon and hydrogen; but some of them appear to be produced from other volatilised compounds, which are subjected to the further action of a red heat within the apparatus.—4. *Resins*, which may be called *empyreumatic resins*, containing but little oxygen, and generally dark-coloured; according to Unverdorben, some of them dissolve both in alcohol and in potash, others only in alcohol, others again only in potash.—5. If the original compound contains nitrogen, ammonia and volatile alkaloïds are also given off, viz. ethylamine and its homologues, together with pyridine, picoline, lutidine, collidine, pyrrol, and others. (See *ВОНЕ-ОИ*, i. 625.)

Coal yields by dry distillation, especially at low temperatures, a very complex distillate, consisting of an acid portion containing phenic or carboic acid, with smaller quantities of rosolic and brunolic acids, a basic portion containing ammonia, phenylamine, benzylamine, and the volatile bases above mentioned, and a neutral portion consisting of benzene and its homologues, together with the hydrides of the alcohol-radicles, amyl, hexyl, and heptyl, which are liquids,—also the solid compounds naphthalene, anthracene or paranaphthalene, chrysene, pyrene, and the paraffins, which probably consist of the hydrides of the higher terms of the series of alcohol-radicles.

As the more volatile products escape, substances of continually diminishing volatility remain behind; and these, as the temperature rises, are either evolved unaltered in the gaseous form, or resolved into more volatile matters and residual products of still greater fixity.

The hydrogen, nitrogen, and oxygen, which finally remain, are either sufficient to form, with the whole of the residual carbon, a compound which is volatile at a higher temperature, in which case nothing remains in the retort; or, the relative quantity of the carbon is too great to enter wholly into such a state of combination; and then, as the heat approaches to redness, this excess remains behind in the form of charcoal, still combined with small quantities of the other substances, which, however, are separated the more completely as the residue is finally subjected to a stronger heat.

Compounds containing a medium quantity of oxygen, such as sugar, gum, wood, and glue, leave, if they are not volatile, the largest quantity of charcoal; because a large portion of the hydrogen, which would otherwise volatilise the carbon, is converted by the oxygen into water. These compounds leave more charcoal in proportion as they are heated more slowly, because the quantity of water formed is then likewise greater. When the proportion of oxygen is large, this element also tends to volatilise the carbon, in the form of carbonic anhydride and carbonic oxide. When the quantity of oxygen is comparatively small, the hydrogen combines chiefly with the carbon, forming volatile compounds, such as gases, oils, camphors, and resins.

If the compound, during dry distillation, passes into a fused or softened state, which is most frequently the case, the charcoal appears inflated, like that formed from resin and sugar, or at all events very porous, like that from tartaric acid and cork. But if the compound, wood, for example, remains solid while subjected to heat, the charcoal still exhibits the original form and internal structure, but is contracted in volume.

Spongy platinum, inasmuch as it favours the formation of vapour in liquids, may cause an organic compound to be completely resolved into volatile products at a lower temperature than it would if heated alone. Thus, tartaric acid mixed with spongy platinum and carefully heated, yields nothing but carbonic acid and a transparent and colourless, crystallisable distillate. (Reiset and Millon.)

The products of dry distillation may be arranged in the following classes, according to their external forms:

1. *Gases*.—Hydrogen and nitrogen;—carbonic oxide, carbonic anhydride, hydrochloric, hydrobromic, hydriodic, and sulphydric acid gases, marsh-gas, olefiant gas, and tetrylene. In this gaseous mixture, the vapours of empyreumatic oils and of sulphide of carbon are also diffused.

2. *Watery distillate*.—The water contained in this distillate was either attached as such to the organic compound, or it has been formed at the high temperature to which that compound has been subjected, from the oxygen and hydrogen contained in it. In this water are dissolved:—*a*. In some few instances, alcoholic fluids, such as aldehyde, wood-spirit, lignone, and acetone.—*b*. Almost always acids, of which the most frequent is acetic acid. Hence the watery distillate obtained in the dry distillation of non-azotised organic bodies almost always has an acid reaction (see ACETIC ACID, i. 9).—*c*. The watery distillate obtained from azotised substances contains small quantities of hydrocyanic acid and large quantities of ammonia, often mixed with compound ammonias, such as methylamine, ethylamine, &c. When the quantity of ammonia is but small, it is completely saturated by the acetic acid or any other stronger acid that may be present, and the watery distillate still exhibits an acid reaction, or is neutral; but in the distillate obtained from most azotised bodies, these stronger acids are not present in sufficient quantity to neutralise the large quantity of ammonia, the excess of which, therefore, unites with the carbonic acid, and in the form of carbonate of ammonia, imparts an alkaline reaction to the liquid. By this character, a non-azotised organic compound may be distinguished from one which contains nitrogen. The former yields an acid distillate, which does not give off ammonia even on the addition of potash; the latter gives either an alkaline distillate, or, if it contains but little nitrogen, a neutral or acid distillate which gives off ammonia when treated with potash. But a non-azotised organic compound likewise yields ammonia by destructive distillation, if it be previously mixed with nitre. Thus, gum-arabic distilled with one-tenth of its weight of nitre yields ammonia



and a pyrophoric charcoal containing cyanide of potassium (Vauquelin, Ann. Chim. lxxii. 59).—*d.* The watery distillate likewise holds in solution a small quantity of the tarry matter next to be considered, which gives it a brown colour.

3. *Oily or Tarry Distillate, Empyreumatic Tar.*—Generally a brown and fetid mixture of different empyreumatic oils, camphors, and resins, which may likewise contain volatile alkaloids, a brown mouldy substance, and another brown substance soluble in water and alcohol, and forming with potash, baryta, and lime, compounds which are soluble in water, and, with the other earths, compounds which are insoluble. The most fetid tar is that obtained from the more highly azotised compounds, such as gelatin and white of egg. The offensive odour of most empyreumatic tars is ascribed by Unverdorben (Pogg. 253, 297, and 477) to a peculiar oily acid which he calls *empyreumatic acid*, which, however, varies with the nature of the original compound, being sometimes lighter, sometimes heavier, than water.

4. *Sublimed Products.*—These products consist sometimes of an acid, *e. g.* pyrogallic acid, sometimes of a camphor, sometimes of carbonate of ammonia.

5. *Charcoal.*

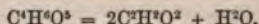
Some organic compounds yield all these products, viz. gases, watery liquid, tar, sublimate, and charcoal. Such is the case with gelatin, albumin, &c., in which the sublimate consists of carbonate of ammonia. Other compounds, as sugar, woody fibre, &c., yield gases, a watery liquid, tar, and charcoal, but no sublimate. (See ACETIC ACID, BONE-OIL, CINCHONINE, COAL.)

The nature of the products obtained by the destructive distillation of any substance, often varies considerably with the temperature to which it is subjected; thus coal, when distilled at bright red heat, yields a large quantity of gaseous, and a comparatively small quantity of liquid hydrocarbons, whereas, when the distillation is conducted at a low red heat, the proportion of liquid products is much greater. The paraffin oils now so largely used for illumination and for lubricating machinery, are prepared by distilling Boghead coal at a low red heat.

We have hitherto spoken chiefly of the decomposition of bodies of complex or indefinite constitution, such as wood, coal, animal matter, &c. The more simply constituted organic compounds, such as acids, bases, and salts, yield by dry distillation, especially if carefully conducted, a small number of products, bearing a definite and, generally speaking, a simple ratio to the original substance. The following are examples:—

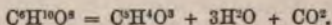
*a. Decomposition of non-azotised organic bodies.*—Many acids are wholly resolved into water or carbonic anhydride (or both together), and one or more acids, called *Pyro-acids*, containing less oxygen.

*Malic acid*, when quickly heated to 200° C., is almost completely resolved into water and maleic acid, which distil over:

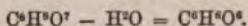


At 150° C., it yields, as principal product, a residue of fumaric acid, which is polymorphic with maleic acid, and may be regarded as a dibasic acid =  $C^4H^4O^4$ . At a more intense heat, the products are carbonic oxide, marsh-gas, empyreumatic oil, and charcoal.

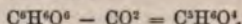
*Mucic acid* is resolved into 1 at. carbonic anhydride, 3 at. water, and pyromucic acid:



*Citric acid*, when heated in a retort, gives off 1 at. water, and leaves a residue of aconitic acid:

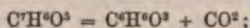


This *aconitic acid*, if more strongly heated in the retort, gives off 1 at. carbonic anhydride and distils over as itaconic acid:

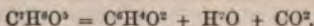


At the same time, another portion of the citric acid is decomposed in a different manner, being resolved into carbonic oxide, acetone, empyreumatic oil, and charcoal.

*Gallie acid*, heated to 210° C., yields carbonic anhydride and a distillate of pyrogallie acid:



but at 250°, it gives off water and carbonic anhydride and leaves metagallic acid:



*Meconic acid* gives off carbonic anhydride, and yields a sublimate of pyromeconic acid:



*Oxalic acid* partly sublimes undecomposed; another portion is resolved into water, carbonic oxide, and carbonic anhydride:



and a third part into formic acid and carbonic anhydride:



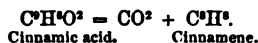
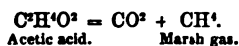
*Salicylic acid*, when quickly heated, is resolved into carbonic anhydride and phenylic alcohol:



*Orsellic acid* yields carbonic anhydride and orcin:

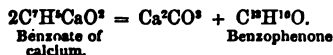
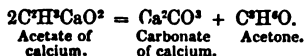


In some cases, the whole of the oxygen of the organic compound is eliminated in the form of water and carbonic anhydride, and hydrocarbons of various composition are produced: thus,



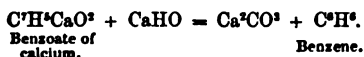
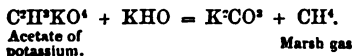
Monobasic acids are, for the most part, resolved by dry distillation into 1 molecule of carbonic anhydride, together with a hydrocarbon (*e. g.* acetic, cinnamic, benzoic acid, &c.), or into carbonic anhydride and an alcohol (like salicylic acid); dibasic acids yield 1 molecule of carbonic anhydride and a monobasic pyro-acid (oxalic acid yields carbonic anhydride and formic acid),—or two mol.  $\text{CO}^2$  and a hydrocarbon, sometimes also water (phthalic acid,  $\text{C}^8\text{H}^4\text{O}^4$ , yields  $2\text{CO}^2$ , and 1 at. benzene,  $\text{C}^6\text{H}^6$ );—and tri-basic acids yield either 1 mol. carbonic anhydride and a dibasic pyro-acid (citric acid yields  $\text{CO}^2$  and itaconic acid), or 2 mol.  $\text{CO}^2$  and a monobasic acid, or 3 mol.  $\text{CO}^2$  and a hydrocarbon.

Under the influence of strong chemical reagents, the decomposition by heat often takes a different form. Thus, organic bodies heated with caustic *alkalis* yield acids as their chief products of decomposition, formic, oxalic, and carbonic acids being frequently produced in this manner; monobasic acids heated with lime or baryta yield acetones, together with a carbonate of the earth-metal, *e. g.*



Sometimes a more complex decomposition takes place, resulting in the formation of hydrocarbons, together with aldehydes, or compounds isomeric therewith, *e. g.* butyral from butyric acid (*i. 689*).

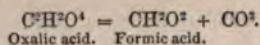
In many cases, when a considerable quantity of lime or baryta, or an excess of hydrate of potassium or sodium is present, the whole of the oxygen of the acid is converted into carbonic anhydride, and a hydrocarbon is given off:



In other cases, organic acids of more simple constitution are produced; thus, oleic acid heated with hydrate of potassium, yields palmitate and acetate of potassium, together with free hydrogen:

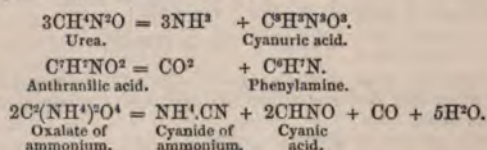


Dibasic acids frequently yield monobasic acids, together with carbonic anhydride: thus,

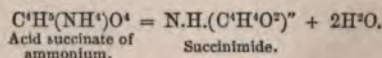
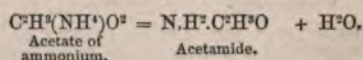


Under the influence of sulphuric acid, phosphoric acid, or chloride of zinc, the elements of water are often withdrawn, and a hydrocarbon produced: thus alcohol,  $\text{C}^2\text{H}^5\text{O}$ , is resolved into water,  $\text{H}^2\text{O}$ , and ethylene,  $\text{C}^2\text{H}^4$ ; and borneol,  $\text{C}^{10}\text{H}^{18}\text{O}$ , into  $\text{H}^2\text{O}$  and borneene,  $\text{C}^{10}\text{H}^{16}$ .

6 *Decomposition of azotised bodies.*—When azotised organic bodies are heated *per se*, the greater part of their nitrogen is given off in the form of ammonia, a volatile organic base, or a cyanogen compound; sometimes also in part as free nitrogen, and in the case of compounds containing nitril ( $\text{NO}^2$ ), as an oxide of nitrogen. A small portion of the nitrogen usually remains united with the charcoal, which is left behind when all the volatile products have escaped. The following are examples of some of the modes of decomposition just mentioned:



Certain nitrogen-compounds (ammonium-salts), when gradually heated, give off all their oxygen in the form of water, and are converted into amides, or nitriles.



Oxalate of ammonium,  $\text{C}^2(\text{NH}^4)\text{O}^4$ , is resolved in like manner into 2 at. cyanogen ( $\text{C}^2\text{N}^2$ ) and  $4\text{H}^2\text{O}$ ; formate of ammonium,  $\text{CH}(\text{NH}^4)\text{O}^2$ , into hydrocyanic acid (formonitrile),  $\text{HCN}$ , and  $2\text{H}^2\text{O}$ ; benzoate of ammonium,  $\text{C}^7\text{H}^2(\text{NH}^4)\text{O}^2$ , into cyanide of phenyl (benzonitrile)  $\text{C}^7\text{H}^2\text{N}$ , and  $2\text{H}^2\text{O}$ .

If the nitrogen-compound likewise contains sulphur, this element unites partly with the ammonium and ammonium-bases evolved, forming sulphides, partly with carbon and the ammonium-bases, forming sulphocyanates of those bases, partly with carbon alone, in the form of sulphide of carbon.

Nitrogen-compounds heated with the hydrates of the alkali-metals, either alone or mixed with lime (potash- or soda-lime), generally give off the whole of their nitrogen as ammonia; in some cases, however, volatile organic bases are likewise given off. Thus, caffeine boiled with potash, gives off methylamine, and cinchonine heated with hydrate of potassium, yields pyrrol, pyridine, picoline, lutidine, collidine, chinoline and lepidine.

**DISULPH-ANISOLIC, -BENZOLIC, -ETHOLIC, -METHOLIC, and -PROPOLIC ACIDS.** See SULPHUROUS ETHERS.

**DITETRYL.** The name given by Berzelius to the hydrocarbon  $\text{C}^4\text{H}^8$ , now called *Butylene* or *Tetrylene*.

**DITHIONIC ACID.** See SULPHUR, OXYGEN-ACIDS OF.

**DIURET.** Syn. with BIURET (i. 600).

**DIVI-DIVI** or *Libidibi*. The husks of *Casalpinia coriaria*, Willd., imported from South America, in the form of dark brown rolls containing a few flat seeds. The outer rind of the husk contains a large quantity of tannin, together with ready-formed gallic acid; the tannin easily yields pyrogallie acid by distillation. (Stenhouse.)

**DOCIMASY** (from *δοκμάζω*, to test). A term synonymous with assaying.

**DOEGLAL.** A compound obtained from dögling train oil, and said by Scharling to be analogous to æthal (hydrate of cetyl).

**DOEGLIC ACID.** See the next article.

**DOEGLING TRAIN OIL.** (Scharling, J. pr. Chem. xliii. 257; Jahresber. d. Chem. 1847-8, p. 367.)—The oil obtained from the bottle-nosed whale, *Balæna rostrata*,



called "dögling" in the Faröe isles, where it is caught. The oil has a specific gravity of 0.868 at 20° C., 0.981 at 11°, becomes turbid at 8°, and deposits a crystalline fat at 0°, more abundantly at -8°. It contains, according to Scharling, 79.9 p.c. carbon, and 13.4 hydrogen, and consists mainly of doeglate of doeglyl, with but a small proportion of glycerides, and no iodine. It dissolves in 2 pts. of boiling absolute alcohol, and in 22 pts. weak alcohol. When exposed to the air it takes up oxygen, becomes heavier and more viscid, and ultimately dries up. It forms a better fuel for lamps than common train oil, and may be freed from offensive odour by leaving it exposed to the sun in contact with water, by shaking it up with thin milk of lime, or by dissolving it in boiling alcohol.

Doegling train oil is a mixture of several fats. On leaving it for some time exposed to a temperature of -8° C., it separates into a liquid oil and a fat which melts at 24° C., contains a small quantity of spermaceti, and yields by saponification a turbid soap containing a small quantity of a fatty acid, isomeric or identical with capric acid,  $C^{10}H^{20}O_2$ . When saponified with oxide of lead, it yields chiefly a lead-salt soluble in ether, with but a small quantity of a lead-salt insoluble therein.

The lead-salt insoluble in ether contains a mixture of a body melting at 49° C. with a smaller quantity of a substance which melts at 100° C. without decomposing. The lead-salt soluble in ether yields, when decomposed by acids, yellow doeglic acid  $C^{10}H^{18}O_2$ , which belongs to the oleic series, is perfectly clear and fluid at 16° C., and solidifies a little above 0° C. It reddens litmus, forms a liquid ethyl-compound,  $C^{10}H^{18}(C^2H^5)O_2$ , and a crystalline barium-salt,  $C^{10}H^{18}BaO_4$ , which dissolves in boiling alcohol and does not melt at 100° C.

Doegling train oil yields by dry distillation a large quantity of a colourless liquid which is a mixture of several fatty acids (including volatile acids like butyric acid), with numerous hydrocarbons. By treating this liquid with carbonate of sodium and water, rectifying it *per se*, treating it with potassium, and again rectifying, a colourless liquid hydrocarbon,  $C^{12}H^{24}$ , is obtained, having a strong aromatic odour, and vapour-density = 5.8 (2 vol.). According to Scharling, this hydrocarbon is formed by the decomposition of oxide of doeglyl,  $C^{12}H^{24}O$ , contained in the oil ( $C^{12}H^{24}O - H^2O = 2C^{12}H^{24}$ ).

Doegling train oil treated with nitrous acid, assumes a darker colour and solidifies; and the solidified oil may be separated by alcohol into a reddish-yellow easily soluble substance, and a colourless, crystallisable, less soluble mass, neither of which has been examined.

**DOG-TOOTH SPAR.** The scalenohedral form of calcspar (i. 722).

**DOLERIN.** A gneissoid rock in the Alps, consisting of talc and felspar.

**DOLERITE.** A rock nearly allied to basalt, and consisting of a crystallo-granular mixture of felspar (labradorite) and augite, with a small quantity of titaniferous magnetic iron ore: it differs from basalt by not containing olivine, and generally also by the absence of zeolites. Its structure varies from small- and fine-grained to compact, seldom coarse-grained. It often contains distinct crystals of augite or labradorite, or both, and then becomes porphyroidal; it likewise acquires an amygdaloid character by the presence of cavities, and is sometimes porous. Specific gravity = 2.75 to 2.99. The essential constituents of dolerite are silica, alumina, lime, magnesia, ferrous and ferric oxide, with small quantities of potash and soda. Dolerite from Iceland, analysed by Auerbach, gave 38.18 per cent. labradorite and 61.32 augite. Dolerite from Meissner, analysed by Heusser (Pogg. Ann. lxxxv. 298), gave 47.60 labradorite and 49.60 augite, and by ultimate analysis 48.00  $SiO_2$ , 16.28  $Al_2O_3$ , 15.55  $Fe_2O_3$ , 9.50  $CaO$ , 3.85  $Mg_2O$ , 2.01  $Na_2O$ , 2.01  $K_2O$ , 2.80 water (loss included).

Dolerite occurs as an eruptive rock in enormous masses, streams, veins, beds, and crusts; it generally weathers somewhat easily; it is but slowly attacked by acids. A very fine formation of coarse-grained dolerite is found at Meissner in Hesse. See D'Aubisson (*Traité de Géognosie*, ii. 558, note).—On the dolerites of the left bank of the Rhine (Bergemann, Karsten's Archiv. xxi. 3; Rammelsberg's Handw. 4, suppl. 49; Jahresber. d. Chem. 1849, 803).—On the dolerite of Guadaloupe (Deville, Bull. géolog. [2] viii. 425; Jahresber. 1851, 862).—On the dolerites of the Siebenbürg (Dechen, Verhard. d. naturalist. Vereins d. preuss. Rheinl. 1852, 3, 4, Heft. 289; Jahresber. 1852, 949).—On the products of decomposition of dolerite (R. Ludwig, Jahresber. 1851, 831).

**DOLOMITE.** The compact and granular varieties of magnesio-calcic carbonate ( $Ca; Mg^2CO_3$ , the crystallised varieties being called Bitter-spar (i. 600). The following sub-varieties have been distinguished:

1st. *Granular Dolomite.*

a. *White granular.* It occurs massive, and in fine granular distinct concretions, loosely aggregated. Lustre glimmering and pearly. Fracture in the large, imperfect

slaty. Faintly translucent. As hard as fluor-spar. Brittle. Specific gravity, 2·83. Effervesces feebly with acids. Phosphorescent on heated iron, or by friction. Its constituents are, 46·5 carbonate of magnesium, 52·08 carbonate of calcium, 0·25 oxide of manganese, and 0·5 oxide of iron (Klaproth). Beds of dolomite containing tremolite occur in the island of Iona, in the mountain-group of St. Gothard, in the Apennines, and in Carinthia. A beautiful white variety, used by ancient sculptors, is found in the Isle of Tenedos.

The *flexible* variety was first noticed in the Borghese palace at Rome; but the other varieties of dolomite, and also common granular limestone, may be rendered flexible by exposing them in thin and long slabs to a heat of 480° Fahr. for six hours.

*b. Brown Dolomite*, or magnesian limestone of Tennant.

Colour, yellowish-grey and yellowish-brown. Massive, and in minute granular concretions. Lustre, internally glistening. Fracture, splintery. Translucent on the edges. Harder than calcareous spar. Brittle. Specific gravity of crystals, 2·8. It dissolves slowly, and with feeble effervescence; and when calcined, it is long in reabsorbing carbonic acid from the air. Its constituents are, lime 29·5, magnesia 20·3, carbonic acid 47·2, alumina and iron 0·8 (Tennant). In the north of England it occurs in beds of considerable thickness and great extent, resting on the Newcastle coal formation. In the Isle of Man, it occurs in a limestone which rests on greywacke. It occurs in trap-rocks in Fifeshire.

To the preceding variety we must refer a *flexible dolomite* found near Tinmouth Castle. It is yellowish-grey, passing into cream-yellow. Massive. Dull. Fracture earthy. Opaque. Yields readily to the knife. In thin plates, very flexible. Specific gravity, 2·54; but the stone is porous. It dissolves in acids as readily as common carbonate of calcium. Its constituents are said to be 62 carbonate of calcium, and 36 carbonate of magnesium. When made moderately dry, it loses its flexibility; but when either very moist or very dry, it is very flexible.

2nd, *Columnar Dolomite*. Colour pale greyish-white. Massive, and in thin prismatic concretions. Cleavage imperfect. Fracture uneven. Lustre vitreous, inclining to pearly. Breaks into acicular fragments. Feebly translucent. Brittle. Specific gravity 2·76. Its constituents are 51 carbonate of calcium, 47 carbonate of magnesium, 1 carbonate of iron. It occurs in serpentine in Russia.

3rd, *Compact Dolomite*, or *Gurkoffite*. Colour snow-white. Massive. Dull. Fracture flat conchoidal. Slightly translucent on the edges. Semi-hard. Difficultly frangible. Specific gravity 2·76. When pulverised, it dissolves with effervescence in hot nitric acid. It consists of 70·5 carbonate of calcium and 29·5 carbonate of magnesium. It occurs in veins in serpentine rocks, near Gurkoff, in Lower Austria.

**DOME.** A term used in crystallography to designate a trimetric, monoclinic, or triclinic prism, whose faces and edges are parallel to one of the secondary axes, in contradistinction to those which are parallel to the principal axis, the term *prism* being for the most part restricted to these latter. (See CRYSTALLOGRAPHY, pp. 145, 151, 157.)

**DOMEYKITE.** *Arsenical Copper*, *Weisskupfererz*.—An arsenide of copper, Cu<sup>3</sup>As, found in the district of Copiapo and the province of Coquimbo, in Chili, in reniform and botryoidal concretions, also massive and disseminated. Hardness = 3 to 3·5. Lustre metallic. Colour tin-white, with a slight yellowish or iridescent tarnish. Fracture uneven. Melts easily before the blowpipe, emitting an odour of arsenic.

*Analyses*.—*a.* Copiapo, province of Coquimbo (Domeyko, Ann. Min. [4] iii. 5).—*b.* Cordilleras of Copiapo (Field, Chem. Soc. Qu. J. x. 289).—*c.* Coquimbo (Field).—*d.* San Antonio mine, Copiapo, mixed with iron pyrites (Domeyko).

	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>
Copper . . .	71·64	71·56	71·48	70·70
Iron . . .	. . .	. . .	. . .	0·52
Arsenic . . .	28·36	28·44	28·26	23·29
Sulphur . . .	. . .	. . .	. . .	3·87
	100·00	100·00	99·74	98·38

A similar mineral from Michipicoten Island, Lake Superior, of reddish-white to bronze-yellow colour, and specific gravity 7·35 to 7·40, is, according to T. S. Hunt (Sill. Am. J. xxv. 406), perhaps a mixture of domeykit and nickelin.

*Condurrite* (i. 1110), must be regarded as a product of the decomposition of domeykit.

**DOMITE.** A greyish variety of clinkstone from the Puy de Dome in Auvergne.

**DONARIA.** The name given by Bergemann (Pogg. Ann. lxxxvii. 608), to an earth which he obtained from the orangite of Brevig in Norway, and supposed at the

time to be peculiar; later investigations, however, by Bergemann himself and by Berlin and Damour, have shown that it is identical with thorina.

**DOPPLERITE.** A pitch-like substance occurring in layers in the peat near Aussee in Styria (Haidinger, Wien. Akad. Ber. ii. 287). It is gelatinous, elastic like caoutchouc, brownish-black, translucent on the edges, has but little lustre, is very soft, and has a specific gravity of 1.089. When exposed to the air, it quickly gives off a large quantity of water, and splits up into black, highly lustrous, sharp-edged brittle lumps, like jet, having a hardness of 2 to 2.5, and specific gravity of 1.466. In this state it burns away but slowly when heated, leaving a white ash. It is insoluble in alcohol and ether, but dissolves almost entirely in caustic potash. According to an analysis by Schrötter (Wien. Akad. Ber. 1849, p. 285), it contains 51.43 carbon, 5.34 hydrogen, and 48.03 oxygen (= 100): according to another analysis by Schrötter, quoted by Kenngott (Handw. d. Chem. 2<sup>e</sup>. Aufl. ii. [3] 484), it contains 48.06 per cent. carbon, 4.98 hydrogen, 1.03 nitrogen, and 40.07 oxygen. The fresh substance, at 18° C., contains 68.22 per cent. water, and after being heated to 100° C., 78.5 per cent. water.

The same substance appears to occur in the peat deposits at the Gonten baths, near Appenzell (v. Tchudi, Wien. Akad. Ber. ii. 274), and in the peat of Berechtsgarden (Gumbel, Jahrb. J. Min. v. Leonhard, 1858, p. 278). The substance from Hagnetswyl in the Canton of St. Gall, described as dopplerite by J. Deicke (Berg. v. Hüttenm. Zeitg. xvii. 383), does not exhibit the same properties.

**DRACENINE, DRACINE, or DRACONINE.** See DRAGON'S BLOOD.

**DRACO MITIGATUS.** An old name of calomel.

**DRACOL.** Laurent's name for ANISOL.

**DRACONIC ACID.** Syn. with ANISIC ACID (i. 300).

**DRACONIDE.** } See DRAGON'S BLOOD.  
**DRACONINE.** }

**DRACONTYL.** A product of decomposition of dragon's blood, identical, according to Blyth and Hofmann, with metastyrol or metacinnamene (i. 982).

**DRACONTYL, or DRAGONYL, CHLORIDE OF.** Laurent's name for a product of the action of chlorine on oil of tarragon (i. 299).

**DRACYL.** A product of decomposition of dragon's blood, identical, according to Hofmann, with toluene or hydride of benzyl (i. 573).

**DRAGONITE, DRAGONITE.** Syn. with ROCK-CRYSTAL.

**DRACONIC ACID.** Syn. with ANISIC ACID.

**DRAGON'S BLOOD.** *Sanguis Draconis.*—A resin, so called on account of its red colour, which exudes from various trees, either spontaneously or from incisions. Three kinds are distinguished in commerce—1. *East Indian dragon's blood*, which is found on the ripe fruits and leaves of several palms of the genus *Calamus*, viz. *C. Rotang*, *C. pectatus*, *C. draco*. 2. *American*, from incisions in *Pterocarpus draco*, indigenous in the West Indies. 3. *Canary dragon's blood*, from *Dracana draco*. According to Pereira, it occurs, in commerce, in sticks or in the reed (*Sanguis draconis in baculis*); in oval masses or drops (*in lachrymis*); in powder; in the tear (*in granis*); in lumps (*in massis*); and in cakes.

Dragon's blood is dark red-brown, opaque, tasteless and scentless, brittle, and yields by trituration a cinnabar or carmine-red powder. When pure, it dissolves, with fine red colour, in alcohol, also in ether, and in oils both fixed and volatile. Alkalis also dissolve it more or less completely.

The composition of dragon's blood varies with its origin; the several commercial varieties are probably mixtures of different compounds. According to Johnstone, (Phil. Trans. 1839, p. 134), the portion of cake dragon's blood which is soluble in alcohol and ether has the composition  $C^{20}H^{20}O^4$ . Herberger (Buchn. Repert. xxxvii. 17; xl. 138) found in 100 pts. of dragon's blood *in granis*: 90.7 red, amorphous, acid resin, which he designates as draconide, 2.0 fatty matter soluble in ether, 3.0 benzoic acid, 3.7 phosphate of calcium, and 1.6 oxalate of calcium.

The alcoholic solution of dragon's blood forms red or violet precipitates with metallic salts (Herberger). The same turns yellow when mixed with sulphuric or hydrochloric acid, and on addition of water deposits a yellow or reddish compound of the acid with the resin. This compound dissolves in a small quantity of water, forming a yellow solution, which is reddened by alkalis. Melandri (Brandes' Archiv. [1828] xiv. 193) regarded the resin combined with sulphuric or hydrochloric acid as an alkalioid, and designated it as draconine, dracenine, or dracine.

Dragon's blood is decomposed by nitric acid. With acid of specific gravity 1.33 it yields oxalic acid; if the acid has been previously diluted with an equal weight of



water, it forms, when heated with the resin, nitrobenzoic acid, together with a non-volatile acid.

Dragon's blood, when gradually heated, melts and gives off, up to  $210^{\circ}\text{C}$ ., a small quantity of acid watery distillate containing acetone and benzoic acid; as the heat increases, the resin swells up and gives off carbonic anhydride and carbonic oxide, while water is formed, and thick white vapours are evolved, which condense in the receiver to a reddish black liquid. The oily distillate contains two hydrocarbons, dracyl and draconyl, the former of which, according to Hofmann, is identical with toluene or hydride of benzyl (i. 573), the latter with metacinnamene or metastyrol (i. 982). Benzoic acid is also obtained, together with a colourless, mobile, oxygenated oil, which is heavier than water, insoluble therein, but soluble in alcohol and ether, and boils at  $200^{\circ}\text{C}$ .; with potash, this oil yields benzoic acid and a compound not further examined. (Glénard and Boudault, *Compt. rend.* xvii. 503; xix. 505.)

Dragon's blood is used chiefly for colouring varnishes, for preparing gold lacquers, for tooth tinctures and powders, and for staining marble, to which it imparts a fine red colour; it is also used, though rarely, in medicine. A spurious kind of dragon's blood is said to be found in commerce, consisting of a mixture of different resins coloured with sandarach.

**DRAWING SLATE.** *Black chalk.*—Colour greyish-black. Massive. Lustre of the principal fracture, glimmering; of the cross fracture, dull. Fracture of the former slaty, of the latter fine earthy. Opaque. It writes. Streak same colour, and glistening. Very soft. Sectile. Easily frangible. It adheres slightly to the tongue. Feels fine, but meagre. Specific gravity, 2.11. It is infusible. Its constituents are, silica 64.06, alumina 11, carbon 11, water 7.2, iron 2.75. It occurs in beds in primitive and transition clay-slate, also in secondary formations. It is found in the coal formation of Scotland, and in most countries. It is used in crayon-painting. The trace of bituminous shale is brownish and irregular; that of black chalk is regular and black. The best kind is found in Spain, Italy, and France. (See *Ure's Dictionary of Arts, Manufactures, and Mines*, ii. 57.)

**DRESELITE.** *Dreicite.*—A baryto-calcic sulphate, occurring in small unmodified rhombohedral crystals, disseminated on the surface and in the cavities of a quartzose rock at Beaujeu, Dep. of the Rhone, also at Badenweiler in Baden. R : R in the terminal edges =  $93^{\circ}$  or  $94^{\circ}$ . Cleavage rhombohedral in traces. Specific gravity = 3.2 to 3.4. Hardness = 3.5. Lustre pearly; splendent on the fractured surfaces. Streak and colour white. According to Dufrénoy (*Ann. Ch. Phys.* [2] lx. 102) it contains 61.73 per cent.  $\text{BaSO}_4$ , and 14.275  $\text{CaSO}_4$ , agreeing with the formula  $\text{Ca}^2\text{SO}_4.8\text{BaSO}_4$ , or  $\text{Ca} \left\{ \begin{array}{l} \text{SO}_4 \\ \text{Ba} \end{array} \right\}^8$ , together with 8.05 carbonate of calcium, 9.71 silica, 2.405 alumina, 1.52 lime, and 2.31 water.

**DRUPACIN.** Buchner (*Repert.* xli. 237) gave this name to a yellow substance deposited from old bitter almond oil. It was said to dissolve in acids and to be precipitated by bases, and was perhaps benzamide.

**DRUSE,** or *Geode*. A rounded nodule of stone containing a cavity lined with crystals.

**DRYABALANOPS CAMPHORA.** The camphor tree of Borneo and Sumatra, which yields borneol and borneene (i. 626). The borneol or Borneo camphor is a white crystalline substance found in cavities of old trees. The borneene is a liquid hydrocarbon, isomeric with oil of turpentine,  $\text{C}^{10}\text{H}^{16}$ , which exudes from incisions in the younger stems.

The tree likewise contains another oil, described by Lallemant, which is obtained by boiling the different parts of the tree, cut up into small pieces, with water, and collecting the oily layer which floats on the surface. It is a viscid reddish oil, having a strong balsamic odour, and turning the plane of polarisation of a luminous ray to the right. It begins to boil at about  $180^{\circ}\text{C}$ . (borneene boils at  $165^{\circ}$ ), but the boiling point quickly rises to about  $255^{\circ}$  and then to  $300^{\circ}$ , at which temperature the whole of the volatile portion has passed over, and there remains a resin amounting to about half the weight of the original oil. The distilled oil is further resolved by repeated fractional distillation (mostly conducted under diminished pressure) into a more volatile oil, boiling from  $180^{\circ}$  to  $190^{\circ}\text{C}$ ., and a less volatile oil, boiling at about  $260^{\circ}$ . Both have the composition  $\text{C}^{10}\text{H}^{16}$ . The crude oil was not found to contain borneol. (Lallemant, *Études sur la Composition de quelques Essences*, *Ann. Ch. Phys.* [3]; lvii. 404.—Gm. xiv. 354.)

**DRYMIS WINTERI,** or *Wintera aromatica*. The bark of this tree, growing in Brazil, is said to be the *Cortex Winteranus*, formerly used as a tonic. It contains, according to Henry (*J. Pharm.* v. 481), in 100 pts. 1.2 volatile oil, 10 hard

acid resin, 9 extractive matter with a little tannin, 1.6 starch, also woody fibre, salts, &c.

According to more recent investigations by Weissbecker, *Cortex Winteranus* is obtained from *Winteranus Canella*, L. (*Canella alba*, ML.), or from some other plant nearly related thereto.

**DSCHUT.** See JUTE.

**DUCKTOWHITE.** The name given by C. U. Shepard (Sill. Am. J. xxviii. 129) to a mineral found in the copper mine near Ducktown, East Tennessee, having a steel-grey colour inclining to bronze, hardness = 5.5, specific gravity = 4.55 to 4.66, and containing, according to R. A. Fisher, 30.7 pts. iron and 26.0 copper, together with sulphur. According to G. J. Brush, it is a mixture of pyrite, chalkosin, malachite, quartz, limonite, &c.

**DUCTILITY.** That property or texture of bodies, which renders it practicable to draw them out in length, while their thickness is diminished, without any actual fracture of their parts. This term is almost exclusively applied to metals.

The words malleability, laminability, and ductility, though often confounded together, and used in a loose indiscriminate way, are really very different. Malleability is the property of a body which enlarges one or two of its three dimensions by a blow or pressure very suddenly applied. Laminability belongs to bodies extensible in dimension by a gradually applied pressure: and ductility is properly to be attributed to such bodies as can be rendered longer and thinner by drawing them though a hole of smaller area than the transverse section of the body so drawn. U.

**DUFRENOYITE.** *Green Iron ore. Kraurite.*—A basic ferric phosphate,  $2\text{Fe}^{\text{O}^3}.\text{P}^{\text{O}^3}$ , or  $3\text{f}^{\text{O}^3}.\text{O}^3.\text{P}^{\text{O}^3}$ , occurring in indistinct trimetric crystals ( $\alpha\text{P} : \alpha\text{P}$  about  $123^\circ$ ), with brachydiagonal cleavage, or in spherical, botryoidal, or kidney-shaped masses, with radiated fibrous structure, and drusy surface. Hardness = 3.5 to 4. Specific gravity = 3.2 to 3.4. Lustre silky, weak. Colour dull leek-green or blackish-green, changing to yellow and brown on exposure. Streak siskin-green. Subtranslucent. Melts easily to a slag before the blowpipe.

Karsten (Arch. f. Bergb. u. Hüttenw. xv. 243) found in a specimen from Siegen in Saxony, 27.72 p. c.  $\text{P}^{\text{O}^3}$ , 63.45  $\text{Fe}^{\text{O}^3}$  and 8.56 water; Vauquelin (Ann. Ch. Phys. xxx. 202) found, in a specimen from Haute Vienne, France, 27.85  $\text{P}^{\text{O}^3}$ , 56.20  $\text{Fe}^{\text{O}^3}$ , 6.76  $\text{Mn}^{\text{O}^3}$ , and 9.29 water, whence the formula  $2(2\text{Fe}^{\text{O}^3}.\text{P}^{\text{O}^3}) + 5\text{H}^{\text{O}}$ ; (calc. 28.0  $\text{P}^{\text{O}^3}$ , 63.1  $\text{Fe}^{\text{O}^3}$ , 8.9 water).—From a more recent analysis by Pisani (Sill. Am. J. [2] xxiii. 423), the formula appears to be  $2(2\text{Fe}^{\text{O}^3}.\text{P}^{\text{O}^3}) + 7\text{H}^{\text{O}}$ .

**DUFRENOYSITE.** A sulphide of copper and arsenic occurring, together with binnite, in the dolomite of the Binnenthal, in the Ober-Wallis, Switzerland. It forms small monometric crystals, sometimes with numerous faces, of dark steel-grey to iron-black colour, opaque, and with metallic lustre. Hardness = 4.5. Specific gravity = 4.6. Heated in a test-tube, it yields a sublimate of sulphide of arsenic; when roasted, it yields arsenious oxide. Before the blowpipe it gives off arsenical fumes, and melts to a black button. With soda, it yields a button of copper.

The composition of this mineral is variously stated. Uhrlaub (*Königst's Uebers.* 1856-1857, p. 173) found in it:

S	As	Cu	Pb	Ag	Fe
27.54	30.06	37.74	2.75	1.23	0.82 = 100.14;

which, when the lead, silver, and iron are replaced by their equivalents in copper, agrees approximately with the formula  $3\text{Cu}^{\text{S}}.\text{S}.\text{As}^{\text{S}}^{\text{S}}$  or  $\text{Cu}^{\text{S}}.\text{As}^{\text{S}}^{\text{S}}$  (calc. 29.70 S, 31.03 As, 39.27 Cu).—Stockar-Escher, on the other hand (*ibid.* p. 176), found in the pure crystals:

S	As	Cu	Ag
32.73	18.98	46.24	1.91 = 99.86;

which agrees nearly with the formula of normal cuprous sulpharsenate,  $3\text{Cu}^{\text{S}}.\text{As}^{\text{S}}^{\text{S}}$ , or  $\text{Cu}^{\text{S}}.\text{As}^{\text{S}}^{\text{S}}$  (calc. 32.60 S, 19.10 As, 48.29 Cu). The latter formula is the same as that of enargite, and if established for dufrenoyite, would show that cuprous sulpharsenate is dimorphous.

The name *dufrenoyite* has sometimes also been applied to binnite (i. 588).

**DULCARMARIN.** Wittstein's name for a base obtained from the stems of the common nightshade, *Solanum Dulcamara*, which he regards as peculiar, and represents by the formula  $\text{C}^{\text{O}}\text{H}^{\text{O}}\text{NO}^{\text{O}}$  (Vierteljahrsschrift, f. prakt. Pharm. i. 364, 495).

**DULCARIN.** Syn. with BITTERSWEET (i. 600).



**DULCIN.** Syn. with DULCITE.

**DULCINAN.** Syn. with DULCITAN.

**DULCITAN.** *Dulcinan*,  $C^6H^{12}O^3$ . (Berthelot, *Chimie organique fondée sur la Synthèse*, Paris, 1860, ii. 207.)—The anhydride of dulcite ( $C^6H^{14}O^4 - H^2O$ ), obtained by heating dulcite for some time to near  $200^\circ C$ ., or by the decomposition of the dulcitanides. It is a very viscid neutral syrup, which volatilises perceptibly at  $120^\circ C$ ., and is partially converted into dulcite by prolonged contact with water, or by heating with water and baryta-crystals. It is soluble in water and in absolute alcohol, but not in ether. The composition of its salts, the dulcitanides, shows that it may be regarded as a tetratomic alcohol,  $\left\{ \begin{smallmatrix} (C^6H^8O)^{iv} \\ H^4 \end{smallmatrix} \right\} O^4$ .

**DULCITANIDES.** Compounds of dulcitan with acids, analogous to the mannitanides and glycerides. They may be regarded as dulcitan, in which 2 or 4 at. H are replaced by acid radicles, or as compounds of dulcitan minus  $H^2O$ , with the corresponding anhydrides; thus, *butyro-dulcitan*  $C^{14}H^{24}O^7 = H^2 \cdot \left\{ \begin{smallmatrix} (C^6H^8O)^{iv} \\ (C^4H^6O)^2 \end{smallmatrix} \right\} O^4 = C^6H^{16}O^4 \cdot C^4H^{14}O^3$ .

They are prepared by heating dulcite with acids in sealed tubes, maintaining the temperature for some time at  $100^\circ C$ ., or more easily by raising it to  $200^\circ - 220^\circ$ . The fused mass is mixed with excess of a strong solution of carbonate of sodium and a little caustic potash, then repeatedly exhausted with ether; the ethereal solution is digested with animal charcoal; and the filtrate evaporated over the water-bath. If the residue is still not quite neutral, it must be again treated with carbonate of sodium and ether.

*Benzodulcitan*,  $C^{20}H^{30}O^7 = H^2 \cdot \left\{ \begin{smallmatrix} (C^6H^8O)^{iv} \\ (C^8H^{10}O)^2 \end{smallmatrix} \right\} O^4$ .—Resinous, of the consistence of turpentine, decomposed by boiling with a mixture of alcohol and hydrochloric acid, yielding benzoate of ethyl; by hydrate of calcium into benzoate of calcium, and a mixture of dulcite and dulcitan.

*Butyrodulcitan*,  $C^{14}H^{24}O^7 = H^2 \cdot \left\{ \begin{smallmatrix} (C^6H^8O)^{iv} \\ (C^4H^6O)^2 \end{smallmatrix} \right\} O^4$ .—Colourless, viscid oil, having a bitter and buttery taste; neutral, sparingly soluble in water, easily in absolute alcohol and in ether. Boiled with alcohol and hydrochloric acid, it yields dulcitan and butyric ether.

*Stearodulcitan. a. Neutral.*  $C^{42}H^{60}O^7 = H^2 \cdot \left\{ \begin{smallmatrix} (C^6H^8O)^{iv} \\ (C^{16}H^{20}O)^2 \end{smallmatrix} \right\} O^4$ .—Nearly white, crystalline, neutral. Closely resembles monostearin, both in its physical and in its chemical characters.

*b. Acid.*  $C^{78}H^{118}O^9 = \left\{ \begin{smallmatrix} (C^6H^8O)^{iv} \\ (C^{18}H^{26}O)^4 \end{smallmatrix} \right\} O^4$ .—Obtained by heating dulcite to  $220^\circ C$ . with a large excess of stearic acid. It is white, neutral, and very much like tristearin.

**DULCI-TARTARIC ACID.**  $C^{14}H^{20}O^{13} = H^2 \cdot \left\{ \begin{smallmatrix} (C^6H^8O)^{iv} \\ (C^4H^6O)^4 \end{smallmatrix} \right\} O^4 \cdot C^4H^6O^3$ , or  $\left\{ \begin{smallmatrix} (C^6H^8O)^{iv} \\ 2(C^4H^6O)^4 \end{smallmatrix} \right\} O^4 + 2H^2O$ . (Berthelot, *loc. cit.*)—Known only as a calcium-salt, which is obtained by heating a mixture of equal parts of dulcite and tartaric acid to  $100^\circ - 120^\circ C$ . for five hours in an open vessel, triturating the resulting glutinous mass with chalk and a little water till it becomes neutral, then filtering, precipitating with alcohol, and purifying by repeated solution in water and precipitation with alcohol. This salt, dried in vacuo, has the composition  $C^{14}H^{18}CaO^{13} + 4aq$ , and gives off its water at  $100^\circ C$ .

**DULCITE.** *Dulcin, Dulcose, Melampyrite, Melampyrin.*  $C^6H^{14}O^4 = \left\{ \begin{smallmatrix} (C^6H^8O)^{iv} \\ H^4 \end{smallmatrix} \right\} O^4 + H^2O$ . (Laurent, *Compt. chim.* 1850, p. 364; 1851, p. 29.—Jacquelin, *ibid.* 1851, p. 21.—Hünefeld, *J. pr. Chem.* vii. 233; ix. 47.—Eichler, *Ueber das Melampyrin*, Moskau, 1855; *Rep. Chim. pure* ii. 103.—L. Gilmer, *Ann. Ch. Pharm.* exxiii. 372.—Erlenmeyer and Wanklyn, *Chem. Soc. J.* xv. 455.)—A saccharine substance similar to and isomeric with mannite. The plant from which it was originally obtained is unknown. It was first sent to Paris in 1848 from Madagascar, in lumps more or less rounded, crystallised throughout their entire mass, and covered externally with earthy particles. It is easily purified by means of boiling water, the filtered solution depositing crystals of dulcite, an additional quantity of which separates from the mother-liquor on standing, while a nearly colourless, uncrystallisable syrup remains.

Quite recently Gilmer has shown that *melampyrite*, the saccharine substance obtained by Hünefeld from *Melampyrum nemorosum*, and by Eichler from *Scrophularia*



*nodosa* and *Rhinanthus Crista Galli*, and hitherto regarded as  $C^{12}H^{18}O^{13}$ , or  $C^{12}H^{20}O^{12}$ , is really identical in composition and properties with dulcite, a result confirmed, so far as the composition is concerned, by the experiments of Erlenmeyer and Wanklyn. It is convenient, however, to retain the name melampyrite, to indicate the origin of the substance.

**Preparation of Melampyrite.**—1. The decoction of the dried herb of *Melampyrum nemorosum*, taken at the flowering time, is mixed with milk of lime till it exhibits an alkaline reaction, then boiled up, filtered, concentrated to a small bulk, and acidulated with hydrochloric acid. On cooling and further crystallisation, melampyrite crystallises out, and may easily be obtained pure by recrystallisation from water (Eichler).—2. The dried herb is boiled with water containing hydrochloric acid; the decoction is strained, mixed with milk of lime till it exhibits a slight alkaline reaction, then concentrated, whereupon it deposits succinate of calcium; and the calcium-compound of melampyrite, which passes into the filtrate, is decomposed with hydrochloric acid; it then deposits crystals, which may be purified by recrystallisation (Eichler).—3. Hünefeld evaporates the decoction to a syrup, and leaves the melampyrite to crystallise out; removes from the mother-liquors the substances precipitable by neutral and basic acetate of lead, and the excess of lead by sulphydric acid; and again evaporates. Eichler, instead of proceeding in this manner, precipitates the decoction with neutral acetate of lead, boils the filtrate with lead-oxide, removes dissolved lead by sulphydric acid, and evaporates.

**Properties.**—Dulcite (from Madagascar) crystallises in colourless highly lustrous prisms of the monoclinic system, having their obtuse edges symmetrically truncated, together with the octahedral and basal end-faces.  $\alpha P : \infty P \infty : +P : -P$ .  $\alpha P$ . Inclination of  $\alpha P : \alpha P = 112^\circ$ ;  $+P : -P = 115^\circ 26'$ ;  $\alpha P : +P = 134^\circ 42'$  (Laurent). Melampyrite (from *Melampyrum nemorosum*) crystallises from moderately warm aqueous solution in transparent colourless, shining, monoclinic prisms, with octahedral summits, the faces of which are truncated by an orthodiagonal dome.  $\alpha P : +P : -P : +P \infty : -P \infty$ . Inclination of  $\alpha P : \alpha P = 112^\circ$ ;  $+P : -P = 116^\circ 46'$ ;  $\alpha P : +P = 134^\circ 50'$  (Gilmer). The crystals from both sources are usually aggregated in crusts. Both are inodorous, have a slightly sweet taste and neutral reaction, and are destitute of optical rotatory power.

Dulcite dissolves in 31 pts. water at  $15^\circ C$ . (Gilmer); melampyrite in 25.5 pts. of water at  $15^\circ C$ ., easily in boiling water (Eichler); in 29.41 pts. water at  $16^\circ C$ . (Gilmer); in 34.41 pts. at  $16.5^\circ C$ . (Erlenmeyer and Wanklyn). Both are but slightly soluble in alcohol, even at the boiling heat, in which respect they differ essentially from mannite. Melampyrite is slightly soluble in acetone, wood-spirit, chloroform, and acetic ether.

Dulcite melts at about  $190^\circ C$ . (Laurent), at  $182^\circ$  (Jacquelin); melampyrite at  $186^\circ$  (Eichler), at  $180^\circ$  (Gilmer).

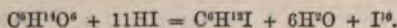
The identity in composition between dulcite and melampyrite is shown by the following analyses:—

			Dulcite.		Melampyrite.	
	Calculation.		Laurent.	Jacquelin.	Gilmer (mean).	Erlenmeyer and Wanklyn.
C <sup>6</sup> . . . . .	12	39.56	39.20	39.69	39.6	39.33
H <sup>18</sup> . . . . .	14	7.69	7.61	7.70	7.9	7.90
O <sup>8</sup> . . . . .	96	52.75	53.19	52.61	52.5	52.77
<u>C<sup>6</sup>H<sup>18</sup>O<sup>8</sup></u>	<u>112</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.0</u>	<u>100.00</u>

Eichler found in melampyrite 37.79 per cent. carbon and 7.83 hydrogen, whence he deduced the formula  $C^{12}H^{18}O^{13}$  [or  $C^6H^{14}O^8 + \frac{1}{2}H_2O$ ]. The substance analysed was perhaps not thoroughly dried.

**Decompositions.**—1. Dulcite heated to  $200^\circ C$ . gives off water, and is converted into dulcitan (p. 348); at  $275^\circ C$ . it decomposes and gives off carbonic oxide without much colouring, and at higher temperatures gives off large quantities of gas, smelling of acetic acid and acetone, and distils without residue (Laurent, Jacquelin). Melampyrite begins to decompose at  $180^\circ C$ . (Eichler), at  $275^\circ$  (Gilmer).—2. Dulcite in solution is slowly decomposed by chlorine, yielding an acid, the barium-salt of which is soluble, but not crystallisable.—3. Dulcite boiled with nitric acid is converted into mucic, oxalic, and racemic acids (Laurent; Carlet, Compt. rend. li. 137; liii. 343). Melampyrite treated in like manner yields mucic and oxalic acids (Eichler, Gilmer); the formation of racemic acid was not observed, probably because the quantity operated upon was insufficient (Gilmer).—4. Fuming nitric acid converts dulcite into hexanitrodulcite (see below). Melampyrite treated with a mixture of nitric and sulphuric acids also yields a nitro-compound.—5. Dulcite and melampyrite both dissolve

in strong sulphuric acid, and on heating the solution an acid is formed, which yields a soluble barium-salt (Laurent, Eichler).—6. Melampyrite heated with *hydriodic acid* in an atmosphere of carbonic acid yields iodide of hexyl, together with water and free iodine (Erlenmeyer and Wanklyn):



7. Dulcite is not decomposed by dilute *potash*; but when heated with strong *potash-ley*, it is converted into a thick, syrupy, colourless mass, the solution of which is not precipitated by alcohol.—8. Dulcite heated with *butyric*, *benzoic*, or *stearic acid* to 200° C. is converted, with elimination of water, into compounds called *dulcitanides* (p. 348), analogous to the *mannitanides*, which are decomposed by water into *dulcitan* and the acid, and by alcohol into *dulcitan* and the corresponding ether. (Berthelot.)

Melampyrite is not decomposed by boiling with dilute acids or alkalis, or by *potassic-nitric tartrate*. It is not altered by boiling with dilute sulphuric acid and acid chromate of potassium, and when mixed with *potash* does not reduce mercuric oxide. (Eichler.)

9. Neither dulcite nor melampyrite ferments with *yeast* (Jacquelain, Eichler, Gilmer). Dulcite left for some weeks at 40° C. in contact with chalk and *cheese*, is resolved, like *mannite*, into alcohol, lactic acid, and butyric acid; in contact with *testicular tissue*, it forms a peculiar sugar. (Berthelot, Ann. Ch. Phys. [3] i. 348, 372.)

*Dulcitates*.—These compounds are formed by the substitution of metals for a portion of the hydrogen in dulcite or melampyrite. Those containing the alkali- and alkaline-earth-metals are soluble in water, the lead- and copper-compounds are insoluble. The aqueous solution of dulcite or melampyrite does not precipitate metallic salts.

*Ammonium-salt*.—Melampyrite crystallises unaltered from aqueous ammonia or after being heated with it to 120° C.; but when *nitromelampyrite* (see above) is decomposed by sulphide of ammonium, or when the barium- or calcium-compound of melampyrite is decomposed by carbonate of ammonia, the concentrated filtrate yields transparent, colourless, rectangular prisms, which have an alkaline reaction, do not give off ammonia at 100° C., but become carbonised at higher temperatures, with loss of ammonia, and without previous fusion, and are decomposed by acids into melampyrite and an ammonia-salt. These crystals are easily soluble in water. (Eichler.)

*Barium-compound*.  $\text{C}^6\text{H}^{12}\text{Ba}^2\text{O}^6 + 8\text{H}^2\text{O}$  or  $\text{C}^6\text{H}^{14}\text{O}^6.\text{Ba}^2\text{O} + 7\text{H}^2\text{O}$ .—When dulcite or melampyrite is heated with water and *baryta-crystals*, a clear solution is formed, which on cooling deposits prismatic crystals. Easily soluble in warm water, less soluble in alcohol, which, however, does not precipitate the aqueous solution. The crystals give off 27.4 per cent. water at 170° C., and contain 29.7 per cent. barium, agreeing with the formula  $\text{C}^6\text{H}^{14}\text{O}^6.\text{Ba}^2\text{O} + 7\text{aq.}$  which requires 27.33 water and 29.71 barium (Laurent). According to Eichler, they give off 26.73 per cent. water at 120° C., and contain 28.5 per cent. barium, whence he deduces the formula  $\text{C}^{12}\text{H}^{13}\text{O}^{13}.2\text{BaO} + 14\text{HO}$  (calc. 26.78 water and 29.16 barium). It was doubtless the same as Laurent's compound, the two formulæ differing indeed only by  $\text{HO}$  or  $\frac{1}{2}\text{H}^2\text{O}$ .

*Calcium-compound*.—Aqueous melampyrite dissolves lime.

*Copper-compound*.—Melampyrite boiled with cupric sulphate and *potash* yields a clear blue solution. From aqueous melampyrite an ammoniacal solution of cupric sulphate throws down a light blue precipitate, which, after washing with weak aqueous ammonia, turns green at 100° C., and contains 55.25 per cent. cupric oxide, agreeing therefore with the formula  $\text{C}^{12}\text{H}^{13}\text{O}^{13}.\text{CuO}$ , which requires 55.49 per cent.  $\text{CuO}$  (Eichler), probably  $\text{C}^6\text{H}^{13}\text{CuO}^6 + \text{H}^2\text{O}$ .

*Lead-salt*.—Aqueous solutions of dulcite and melampyrite are not precipitated by acetate of lead either neutral or basic. From an ammoniacal solution of the neutral acetate, aqueous melampyrite throws down a white precipitate which, after drying at 100° C. in a stream of hydrogen, contains 77.68 per cent.  $\text{PbO}$ , answering to the formula  $\text{C}^{12}\text{H}^{13}\text{O}^{13}.6\text{PbO}$  (calc. 77.84  $\text{PbO}$ ) (Eichler); probably  $\text{C}^6\text{H}^{12}\text{Pb}^2\text{O}^6.2\text{Pb}^2\text{O} + \text{aq.}$

*Potassium-salt*.—Warm alcoholic *potash* dissolves melampyrite, and the solution when left to itself deposits needles which have a caustic alkaline taste, are easily soluble in water, absorb water and carbonic acid from the air, and are converted into a mixture of melampyrite and carbonate of potassium. (Eichler.)

*Sodium-salt*.—Small flat needles resembling the potassium-salt, but less soluble in alcohol. (Eichler.)

*Nitro-derivatives of Dulcite.*

**HEXNITRODULCITE**,  $C^6H^4(NO_2)^6O^4$ .—A solution of dulcite in 5 pts. fuming nitric acid is mixed with 10 pts. oil of vitriol, and the mixture, which becomes turbid, is immediately thrown into a large quantity of water. The semifluid precipitate solidifies slowly to a buttery mass, which, after washing with water, may be crystallised from alcohol. It forms beautiful, colourless, flexible needles, which melt between  $68^\circ$  and  $72^\circ$  C., give off nitric acid vapours continuously, and are in the end wholly converted into tetranitrodulcite. When heated to  $90^\circ$  C. it is converted, with regular emission of red vapours, into a pasty mass, and then into a hard, friable, white acid product. (Béchamp, *Compt. rend.* li. 257.)

**TETRANITRODULCITE**,  $C^6H^{10}(NO_2)^4O^4$ .—Hexnitrodulcite is completely converted into this compound, without alteration of crystalline form, by the spontaneous decomposition which it undergoes, with evolution of nitrous vapours, when kept for a month between  $30^\circ$  and  $45^\circ$  C.

Tetranitrodulcite forms needles harder and less flexible than those of hexnitrodulcite, and crystallises from alcohol in beautiful translucent prisms, melts to a pasty mass at  $130^\circ$  C., completely at  $140^\circ$ , and gives off red fumes at  $146^\circ$ .—It is reduced by ferrous salts and forms a non-crystallisable syrup, probably dulcitan. (Béchamp, *loc. cit.*)

**Dulcisulphuric Acid.** *Melampyro-sulphuric acid.*—Melampyrite dissolves in strong sulphuric acid; and the solution diluted with water, saturated with carbonate of lead, filtered from sulphate of lead, and decomposed by sulphydric acid, then filtered from the sulphide of lead and evaporated, yields melampyro-sulphuric acid in the form of a syrup which has a faint yellow colour, a sour and bitter taste, and carbonises when heated, with evolution of sulphurous anhydride.

**Barium-salt.** Obtained by neutralising the acid with carbonate of barium and evaporating the filtrate at a very gentle heat. In the moist state it is a mass having the consistence of turpentine; after drying in vacuo, it forms a transparent gum, which dissolves in water, is precipitated by alcohol, and decomposes at  $100^\circ$  C. According to Eichler's analysis, it contains 36.46 per cent. baryta, and 37.79 sulphuric anhydride, whence he deduces the formula  $C^6H^{12}Ba^2O^{12}.6SO^2$  (calc. 36.26 BaO and 37.86  $SO^2$ ); probably  $C^6H^{11}Ba^2O^{12}.3SO^2$ .

The calcium-salt resembles the barium-salt, but is not precipitated by alcohol from its aqueous solution. The solution does not precipitate acetate of lead, mercurous nitrate, or nitrate of silver. (Eichler.)

Similar results are obtained with dulcite (p. 349).

**DULCONE.** Syn. with DULCITE.

**DUMASIN.** *Pyroacetic oil.*  $C^8H^{10}O$ .—A volatile oil, isomeric with oxide of mesityl, obtained, together with acetone, by the destructive distillation of acetates. It was discovered by Kane (Pogg. Ann. xliv. 494), who assigned to it the formula  $C^8H^8O$ , further examined by Heintz (*ibid.* lxxviii. 277), who regarded it as identical with oxide of mesityl, and afterwards by Fittig (Ann. Ch. Pharm. cx. 21), who confirmed Heintz's formula, but showed that dumasin is not identical, but only isomeric, with oxide of mesityl.

Dumasin cannot be completely separated from the acetone which accompanies it by fractional distillation. Heintz obtains it by distilling 2 pts. acetate of lead with 1 pt. lime; agitates the distillate repeatedly with water, to remove acetone; dries it over chloride of calcium; then decants, and boils it for some minutes in contact with the air; distils till the boiling-point, which is  $130^\circ$  C. at first, rises to  $200^\circ$ , a blackish tar then remaining; and again distils, separating the more volatile portion, which is pure dumasin.

Dumasin is an oil boiling between  $120^\circ$  and  $125^\circ$  C., lighter than water and insoluble therein, but dissolving in alcohol in all proportions. It forms crystalline compounds with the acid sulphites of the alkali-metals, whereby it is distinguished from oxide of mesityl. The sodium-salt contains, according to Fittig,  $C^8H^8NaSO^3 + 3$  aq.

Strong nitric acid converts dumasin into oxalic acid; the dilute acid scarcely acts upon it. Dumasin distilled with hydrochloric acid and peroxide of manganese yields a colourless chlorinated oil,  $C^8H^8Cl^2O$ , heavier than water, boiling between  $150^\circ$  and  $155^\circ$  C., not capable of uniting with acid sulphites of alkali-metals.

**DUMASITE.** Delesse's name for a mineral found in the Vosges, in green scales resembling chlorite. (Dufrénoy, *Traité de Minéralogie*, iii. 790.)

**DUMERILLIA.** The root called *Raiz del Pipitzahuac*, used in Mexico as a purgative, is obtained according to Ramon de la Sagra (*Compt. rend.* xlii. 873,



1072) from *Dumerillia Humboldtii*, Less. It contains a peculiar acid called by him riolozië, by Weldt (Ann. Ch. Pharm. xcv. 188) pipitzahoic acid.

**DYEING.** The art of dyeing consists in fixing upon cloth of various kinds any colours that may be required, in such a manner that they shall not be easily altered by those agents to which the cloth will most probably be exposed.

The most remarkable general fact in the art of dyeing consists in the different degrees of facility with which animal and vegetable substances attract and retain colouring matter, or rather the degree of facility with which the dyer finds he can tinge them with any intended colour. The chief materials of stuff to be dyed are, wool, silk, cotton, and linen, of which the former two are more easily dyed than the latter. This has been usually attributed to their greater attraction to the tinging matter.

Wool is naturally so much disposed to combine with colouring matter, that it requires but little preparation for the immediate processes of dyeing, nothing more being required than to cleanse it, by scouring, from a fatty substance, called the yolk, which is contained in the fleece. For this purpose an alkaline liquor is necessary; but as alkalis injure the texture of the wool, a very weak solution may be used; if more alkali were present than is sufficient to convert the yolk into soap, it would attack the wool itself. Putrid urine is therefore generally used, as being cheap, and containing a volatile alkali, which, uniting with the grease, renders it soluble in water.

Silk, when taken from the cocoon, is covered with a kind of varnish, which, because it does not easily yield either to water or alcohol, is usually said to be soluble in neither. It is therefore usual to boil the silk with an alkali, to disengage this matter. Much care is necessary in this operation, because the silk itself is easily corroded or discoloured. Fine soap is commonly used, but even this is said to be detrimental; and the white China silk, which is supposed to be prepared without soap, has a lustre superior to that of Europe. Silk loses about one-fourth of its weight by being deprived of its varnish. (See BLEACHING.)

The intention of the previous preparations seems to be of two kinds. The first, to render the stuff or material to be dyed as clear as possible, in order that the aqueous fluid to be afterward applied may be imbibed, and its contents adhere to the minute internal surfaces. The second is, that the stuff may be rendered whiter and more capable of reflecting the light, and, consequently, enabling the colouring matter to exhibit more brilliant tints.

Substances which serve to fix colouring matters on vegetable or animal fabrics are called mordants. An essential quality of a mordant is, that it be soluble in water; the mordants most frequently used are the solutions of certain metallic salts.

A mordant acts either by forming an insoluble compound with the colouring matter, which compound is precipitated on or within the fibre, or by modifying the surface of the fibre in such a manner as to enable it to retain the colour.

The decoctions of many dye-stuffs, as well as the solutions of the pure colouring matters prepared from them, form with certain saline solutions coloured precipitates called lakes, consisting of the colouring matter combined with the base of the salt. Many of these lakes are prepared on the large scale and used as pigments. The salts chiefly used for their preparation are the salts of aluminium and the stannic salts; the oxides precipitated from these salts being colourless, the lakes which they produce take exactly the tints of the colouring matters used. Ferric salts are also used for the preparation of lakes, but the precipitates which they form differ considerably in colour from the colouring matters used, being for the most part of duller hue.

In the aluminic, stannic, and ferric salts, the base and acid are held together by a comparatively feeble affinity, so that the precipitation of the base by a colouring matter is generally effected without much difficulty. This however depends upon a variety of circumstances, among which the nature of the acid is of considerable importance; acetate of aluminium or ferric acetate, for example, is much more easily decomposed by colouring matters than the corresponding sulphate. Hence a mixture of alum with acetate of lead is often used as a mordant. Precipitation is often greatly accelerated by heat; many mixtures of metallic solutions with colouring matters, which remain clear in the cold, yield precipitates on boiling. In many cases, however, the addition of a precipitant is necessary to produce the required decomposition; thus a solution of alum mixed with certain colouring matters remains clear, but on adding an alkali, a precipitate is formed consisting of an alumina lake. By this means, lakes may be formed from metallic solutions, which would not yield them with colouring matters alone, such as salts of magnesia, zinc, lead, and mercury.

The formation of insoluble lakes is the principal function of the mordants used in dyeing and calico-printing: nevertheless the number of metallic salts that can be used as mordants is much smaller than that of the salts which are capable of forming lakes, because the applicability of any salt as a mordant depends also on the effect which the

saline solution produces on the fibre to be dyed, and on the behaviour of the fibre saturated with the mordant in the subsequent stages of the process.

Metallic salts are sometimes separated from their solutions by animal or vegetable fibres immersed in them and deposited thereon without decomposition. Wool or silk immersed in a solution of alum takes up a considerable quantity of the salt without decomposing it, so that the alum may be afterwards dissolved out by boiling water, though only after being treated therewith ten times or more in succession. Linen and cotton likewise take up alum from its solution, but only in very small quantity.

The direct separation of a salt from its solutions by organic fibre, is however of much less importance in dyeing than the decomposition of the salt into an acid and a basic salt, and the precipitation of the latter on and within the fibre while the former remains in solution. Stannic chloride is resolved, by boiling its aqueous solution, and under other circumstances, according to the mode of its preparation, into hydrochloric acid and a precipitate of stannic hydrate. Easily soluble ferrous salts are converted, by absorption of oxygen, into insoluble basic ferric salts, which also attach themselves to the fibre. Aluminium-salts containing weak acids, such as the acetate, are easily converted into sparingly soluble basic salts, either by the evaporation of a portion of their acid on exposure to the air (as with the acetate), or by precipitation with the aid of heat. It is this disposition to form basic salts, added to the tendency of the bases to unite with colouring matters, that renders the salts of aluminium, tin, and iron so peculiarly adapted for the fixing of colouring matters. Other substances are however used as mordants, viz. soap, acids, albumin, gluten, tannin, &c.

It is evident that when a mordant is applied over the whole surface of a fabric, and this is afterwards immersed in a dye-bath, it will receive a tint all over its surface; but if the mordant is applied only in parts, the colour will be fixed on those parts only. The former process constitutes the art of dyeing, properly so called; the latter the art of printing colours on stuffs, usually called calico-printing. To produce this topical fixation of the colour, either the mordant is first applied to the entire surface, and then removed in parts by the application of a suitable solvent; or, more frequently, the mordant is mixed with a thickening material, such as gum, starch, paste, albumin, &c., and printed on the parts which are to take the colour; or thirdly, the mordant, thickening materials, and colouring matter, are mixed and printed together on the cloth.

The mordanted cloth has to be submitted to certain preliminary operations before it is ready for dyeing,—first to fix the mordant on the fibre, and secondly to remove superfluous mordant. For fixing the mordant the chief agent employed is heat, which, as already observed, facilitates the separation of the base of the mordant from the acid. Cotton goods are subjected to a treatment called “ageing,” which formerly consisted in hanging them up for several days in a warm room, whereby the acetic acid of the mordant was volatilised, and in the case of iron mordants, the iron was brought to the state of sesquioxide. The change is now however much more quickly effected by the joint action of heat and moisture, the pieces of calico being passed over and under a series of rollers, in a narrow room into which a small quantity of steam is suffered to issue, the temperature being kept at 80° to 100°, or rather more, of Fahrenheit, by means of steam pipes. The aqueous vapour perhaps acts by facilitating the volatilisation of the acid.

The removal of the unfixed or superfluous mordant (and thickening matter in the case of printed goods), is a very important operation, as the excess, if suffered to remain, would consume to no purpose a certain portion of the dye-stuff, and moreover, in printed goods, it would, on immersion in the dye-bath, spread itself over the ground or unprinted portion of the surface, and cause it to take up the colour when it ought to be left white. The cleansing is effected sometimes by simple washing in water, either hot or cold; this is especially the case with fabrics which are to receive a uniform colour, and do not require the mordant to be dried before dyeing. For printed stuffs this simple washing will not suffice; for the superfluous mordant, as it dissolved in the water, would be likely to impregnate the ground and render the pattern indistinct. Hence it is necessary to wash the piece with a solution which will at once decompose the superfluous mordant. This is effected by various means, viz. by the chalk-bath, bran-bath, cowdung-bath, &c. Chalk acts simply by precipitating the alumina or other oxide in the mordant. The action of cowdung, which is especially used for madder goods, has been ascribed to a peculiar acid, also to phosphates, silicates, and other salts. That the latter is the more correct view is proved by the fact that the dung-bath is now almost wholly superseded by the solutions of certain salts, viz. the double phosphate of soda and lime, arsenite and arsenate of soda, and silicate of soda,—all of which act by precipitating the base of the mordant in the form of an insoluble salt which will not unite with the colouring matter or with the fibre.



The manner in which colouring matters are fixed on organic fibres by means of mordants is well illustrated by the following observations of Walter Crum (*Chem. Soc. J.*, vol. xvi. Jan. 1860) on the dyeing of cotton.

When ripe cotton fibre, which consists of an aggregate of fine cylindrical tubes, is immersed in a solution of ferric acetate, a portion of the solution enters the tubes, and on subsequent exposure to a warm moist atmosphere, the acetic acid evaporates and oxide of iron is deposited within the fibre; when the cotton thus mordanted is immersed in a madder bath, a portion of the solution enters the fibre, and the colouring matter unites with the oxide of iron. A similar action takes place when acetate of alumina is used as the mordant. When the cotton is first immersed in subacetate of lead and then exposed to moist warm air, a deposition of oxide of lead takes place within the fibre, and on subsequently dipping it in a solution of chromate of potassium a yellow deposit of chromate of lead is obtained. In like manner, by first steeping the cotton in a solution of tannin, then, after exposure to the air, in a ferric salt, a black precipitate of ferric tannate is formed within the fibre. A piece of dyed cotton may, in fact, be described as a set of colourless bags containing coloured substances, and in so far resembling the natural colours of flowers.

Cotton fibre in the unripe state, in which it has the appearance of flattened blades, but really consists of flattened tubes with extremely narrow bore, is impervious to liquids, and therefore will not take a dye. Such cotton is called *dead cotton*. White fibres consisting of it may frequently be observed in the middle of the coloured portions of printed calicoes.

Various methods are resorted to for forming precipitates within the fibre. Sometimes the fibre is first made to absorb tannin, then treated with an acid solution of tin; in this manner a precipitate of tannate of tin is formed within the fibre, which forms a good mordant for Lima or Brazil wood. When cotton is soaked in a cold weak solution of oxychloride of tin, or better in a mixture of stannous and stannic chlorides, and then immersed in basic ferric chloride or nitrate, a large quantity of iron is deposited within the fibres, probably as ferric stannate. This mordant, when dyed in ferropurssic acid, forms a prussian blue of the greatest richness and brilliancy.

Some colours fix themselves within the fibre without the aid of mordants. Blue indigo, which is insoluble in water, is converted into soluble white indigo by the action of reducing agents, such as ferrous sulphate, orpiment, &c. The solution thus obtained is absorbed by the fibre, and accumulates or becomes precipitated on or within it in the insoluble state; and on subsequent exposure to the air the white indigo is reconverted into blue indigo by oxidation.

Besides the precipitation which takes place within the fibre, there is likewise a considerable quantity of dye deposited in the interstices between the fibres. This portion is less firmly fixed than the former, and is removed by the process of soaping, to which some dyed and printed goods, the madder-purples for instance, are subjected; but in the numerous class of colours which do not require, and indeed would not bear, the soaping process, this external dye is allowed to remain, and contributes greatly to the richness of the tone; such is the case with goods dyed with garancin, the indigo-dye, and all colours fixed by steam. (Crum.)

*Steam-colours.*—This is a style of calico-printing in which one or more mordants are mixed with dye-wood decoctions or other coloured solutions, and printed on the cloth, and then subjected to the heat of a steam-bath, which causes the mordant to unite with the colouring matter and both with the cloth. Superior colours are produced by mordanting the cloth first so as to fix oxide of tin on the fibre.

*Pigment-printing.*—In this style of calico-printing, the same pigments may be used as in oil-painting, and are mechanically fixed to the cloth by a species of cementing. The first fixing agent used was a solution of caoutchouc in naphtha, but this was soon abandoned, chiefly on account of the danger of fire which it occasioned. The fixing materials now used are *albumin*, either of eggs or of blood; *lactarin*, which is prepared from buttermilk by separating the solid part, purifying it from butter and free acid, and then drying it; *gluten*, which is the residue of starch-making from wheat-flour by the simple washing process, the gluten being afterwards dried at a gentle heat; and *tannin*. The albumin coagulates readily at the steam-heat; lactarin and gluten require a small quantity of alkali to dissolve them: they then coagulate by heat like albumin.

Formerly but few colours were printed in this manner, chiefly ultramarine blue and carbon-drab; lately, however, Guignet's chrome-green has been used for pigment-printing, and likewise the aniline colours, which may be fixed with tannin. (See p. 357.)

The various colours which the dyer has to produce are either the primitive colours,



red, blue, and yellow, or combinations of them. Many of the compound tints may however be produced directly by the use of particular dyes—purple, for example, by archil, and by some of the aniline dyes. The following is a brief summary of the principal methods of producing the various colours.

#### RED.

Red of various shades is produced by madder and the products obtained from it, garancin, alizarin, flower of madder, &c., with a mordant of acetate of alumina. (See **MADDER**.)

*Turkey-red* is a madder colour. To produce it, the tissue is first heated in a bath of oil, water, and carbonate of soda (2 parts of the salt to 100 oil), which forms on the surface a modified oil capable of acting as a mordant. It is then dried, freed from excess of fatty matter by pearlash mordanted in a bath of gall-nuts and alum, then immersed in a hot bath containing chalk. After this it is dipped in the madder-bath for 3 hours, the bath being kept at the boiling heat for the first quarter of an hour only. It is next washed, again treated with galls and alum, and dipped in a second bath of chalk and madder, after which it is submitted to the *clearing* operation (*avivage*). For this purpose it is first boiled in a bath of soap and pearlash contained in a closed vessel, then twice in a bath of soap and protochloride of tin. Lastly it is passed through a bath of sour bran, and then exposed to the air. (Pelouze and Frémy.)

*Scarlet* is produced by cochineal with a mordant of stannic chloride, obtained by treating tin-foil with dilute nitric acid and sal-ammoniac.

*Brazil-red*.—Brazil-wood with an aluminous mordant. It is applied chiefly to silks, but is rather fugitive, being destroyed by acids and changed to amaranth by alkalis.

*Lac-dye* is a splendid scarlet imported from India, and prepared from stick lac. Messrs. Haworth and Brooke of Manchester obtained a superior colour by treating stick lac with weak ammonia, and mixing this solution with chloride of tin, whereby a fine red insoluble matter is precipitated.

For the aniline reds, see page 366.

#### BLUE.

*Indigo*.—This blue dye-stuff is first converted into white indigo and rendered soluble, by the action of alkalis and reducing agents, such as protosulphate of iron, opiment, glucose, &c.; the cloth or fibre is then immersed in the solution, and afterwards exposed to the air, the white indigo being thereby oxidised and converted into blue indigo, which thus becomes fixed upon the tissue. To produce white patterns on a blue ground, the pieces are printed before dyeing with what is called a "reserve," that is a composition which prevents the colour from fixing itself on the fibre; the substance most frequently used for the purpose is sulphate of copper, which acts by prematurely oxidising the indigo.

Indigo combined in various proportions with sulphuric acid forms *Sulphindigotia acid*, *Indigo-carmin*, *Saxony blue*, &c.

*Prussian Blue*, *Turnbull's Blue*, &c.—The stuff or fibre is immersed first in a solution of an iron-salt, then in a bath of yellow or red prussiate (pp. 227, 244). In calico-printing, the pattern is sometimes printed with a mixture of yellow prussiate and tartaric acid, or sulphuric acid and alum, and exposed to the action of a hot steam-bath. By this treatment, ferroprussic acid is first set free, and then decomposed by the heat, yielding Prussian blue (p. 227).

*Logwood-blue*.—Produced by decoction of logwood on stuffs mordanted with alum and cream of tartar. The colour is not very stable. Sometimes a light sky-blue tint is first given with a weak bath of indigo, and the colour afterwards deepened by logwood, and brightened by immersion in a bath of protochloride of tin, alum, and tartar.

*Coal-tar blues*.—1. *Asuline*. This fine colour, which was first prepared by Messrs. Guinon, Marnas, and Bonnet of Lyons, is obtained from phenic or carbohic acid by a process which is kept secret. When pure it forms copper-bronze crystals, soluble in alcohol, to which it imparts a splendid blue colour, slightly tinged with red. To dye silk or wool with this colour, the alcoholic solution is added to an acidulated lukewarm bath of water, and the silk or wool is worked in it till it acquires a purple shade of a certain depth. It is then transferred to another bath of boiling water strongly acidulated with sulphuric acid, whereby the purple colour is dissolved, and a most brilliant and permanent blue is left on the material. The dyed silk or wool is then washed repeatedly, passed through a bath containing a little tartaric acid, and dried.

2. *Bleu de Paris* is produced from aniline by the action of corrosive sublimate;—

3. *Bleu de Mulhouse* from *rosaniline* (*Magenta*) by the action of reducing agents.

4. *Chinoline blue* is a finelight blue obtained by the action of iodide of amyl on chinoline, a base contained in coal-tar naphtha, and also produced by the destructive distilla-

tion of cinchonine (i. 869). The chinoline blue obtained from the cinchonine base is a fast colour; but unfortunately that obtained from coal-tar cinchonine is very unstable. (Greville Williams.)

*Ultramarine*.—This splendid blue colour is not used as a dye, properly so called, but only as a pigment in calico printing (p. 354).

#### YELLOW.

*Weld*.—A bright yellow dye is produced by *weld*, the colouring matter of *Reseda luteola*. Cotton to be dyed with it is mordanted with acetate of alumina: silk and wool with alum and tartar.

*Fustic*.—There are two distinct yellow dyes known by this name, viz. *old fustic*, the *bois jaune* of the French, which is obtained from dyer's mulberry (*Morus tinctoria*), and *young fustic*, from the Venetian sumach (*Rhus cotinus*). The former yields, with aluminous mordants, a yellow colour, which is durable, but not very bright; it is used chiefly for mixed tints; the latter yields, with alum or stannic chloride mixed with tartar, a beautiful bright yellow dye, much used in calico-printing. It is changed to a fine purple by alkalis, and the decoction forms an orange-red precipitate with acetate of copper or lead.

*Quercitron*.—The decoction of quercitron (*Quercus nigra*) produces on cotton and wool mordanted with stannic chloride or alum, a yellow colour, which is apt to change to a rusty red; it is also applied as a steam colour, thickened with gum-arabic and mordanted with alum.

*Chromate of Lead*.—The stuff or fibre is immersed first in a bath of basic acetate of lead, then, after washing, in a rather dilute solution of chromate of potassium. The yellow colour thus produced is heightened by immersion in dilute acetic acid, which removes any excess of basic acetate of lead. The neutral acetate and nitrate of lead are also used, and produce at once a fine yellow dye. By immersing the stuff thus dyed in lime water, a basic chromate of lead is formed of a fine orange colour (i. 934).

*Picric Acid*.—This compound, produced by the action of nitric acid on indigo, phenic acid, aloes, gum-resins, &c., was first introduced as a yellow dye about six years ago by Messrs. Guinon, Marnas, and Bonney, silk-dyers of Lyons; it forms a very beautiful and permanent colour.

#### Colours intermediate between Blue and Red: CRIMSON, PINK, CHERRY-COLOUR, &c.

Wool mordanted with alum and cream of tartar may be dyed *crimson* by immersion in a bath of cochineal containing a little tartar. For *amaranth*, which inclines more to blue, the wool is first dyed with logwood mordanted with alum and tartar or chloride of tin, and then with cochineal.

The special dyes for producing these colours are:

1. *Safflower*, the red colouring matter of the flowers of *Carthamus tinctorius*. It is chiefly used for silk, and produces very beautiful but rather fugitive colours. For the mode of applying it, see page 808, vol. i.

2. *Madder* mordanted with a mixture of acetate of alumina and acetate of iron.

3. *Rosaniline*, *Fuchsine*, or *Magenta*.—This splendid dye, which has nearly superseded all others for the production of rose or cherry colour, is obtained from aniline by the action of certain oxidising agents, viz. stannic chloride or mercurous nitrate. It is an organic base, which forms several definite and beautifully crystallised salts. The acetate, which is the salt chiefly used, crystallises in beautiful dark green octahedrons, having a lustre like the wing-cases of beetles. Silk or wool is dyed with it by simply adding some of the colour to a slightly acidulated bath. Its dyeing power is so great that 10 grains will dye 2 square yards of silk. (See ROSANILINE.)

*Roseine* is another crimson or rose-coloured dye, produced, though in small quantity, in the preparation of aniline purple. It may be prepared by the action of peroxide of lead or of manganates on aniline.

**VIOLETS AND PURPLES.**—These colours may be produced by the successive use of logwood and cochineal, the cloth or fibre being first dyed blue with logwood, then passed successively through two cochineal baths mordanted with alum and tartar. The special dye-stuffs for producing them are:

1. *Madder*, *garancin*, or *alizarin*, mordanted with dilute iron-liquor.

2. *Archil* or *Orchil*.—This dye-stuff, obtained from various lichens by maceration in putrid urine or other alkaline liquors, has long been used for the production of violets, mauves, &c., of various shades, but the colours obtained with it were fugitive. It has, however, been shown by M. Marnas of Lyons that a fine purple colour, capable of withstanding the action of acids and of light, may be obtained by treating the lichens with milk of lime, filtering the lime-liquor, and precipitating the colouring matter from it with hydrochloric acid, washing the precipitate on a filter, dissolving it in

caustic ammonia, and keeping this ammoniacal liquor at a temperature of 153° to 160° F. for twenty to twenty-five days. The colouring principles of the lichens then fix ammonia and oxygen, and are transformed into a new series of products, which may be separated from the coloured liquid by chloride of calcium. A fine purple lake is then deposited, which, after being washed and dried, is sold as *French purple*. Salts of alumina, tin, &c., might also be used as precipitants instead of chloride of calcium. French purple dyes silk and wool more readily than common archil. The lake is mixed with an equal quantity of oxalic acid, boiled with water and filtered, oxalate of calcium then remaining on the filter, while the colour passes into the filtrate. This liquid is then added to a slightly ammoniacal dye-bath, and the silk, wool, or cotton mordanted with albumin, or cotton prepared for Turkey-red, is immersed in it, these fabrics then becoming dyed with magnificent fast shades of purple or mauve.

*Murexide or Roman Purple*.—This substance, produced by the action of ammonia on alloxan, was first used as a dying material for silk and wool by MM. Depouilly, Lauth, Meister, Petersen, and A. Schlumberger, in 1856. When mixed with corrosive sublimate, acetate of sodium, and acetic acid, it produces various shades of red and purple. For printing, a mixture of murexide with nitrate of lead and acetate of zinc, properly thickened, is applied to cotton fabrics, which are then left to dry for a day or two, when the colour is fixed by passing the fabric through a mixture of corrosive sublimate, acetate of sodium, and acetic acid. The uric acid, the raw material whence the murexide is prepared, is extracted from guano.

*Aloes*, the resin obtained from the *Aloe socotrina*, has of late been used by the French dyers for producing violets, pinks, maroons, and other shades.

*Aniline-purple*, or *Mauve-dye* (also called *Tyrian purple*, *Phenamine*, *Indisine*).—This colouring matter, which has to a great extent superseded all other purple dyes, was discovered by Mr. W. H. Perkin in 1856. It is prepared by the action of acid chromate of potassium on sulphate of aniline. When pure, it is a brittle substance, with a bronze-coloured surface, sparingly soluble in cold water, to which, however, it imparts a deep purple colour, more soluble in hot water, freely soluble in alcohol and in aniline. It is slightly basic, dissolves in strong sulphuric acid, and is precipitated from its aqueous solution by alkalis and saline substances. With tannin it forms a precipitate insoluble in water, soluble in sulphuric acid. Its colour is not affected by light, or by acids or alkalis. To dye silk with it, the alcoholic solution of the dye is mixed with about eight times its bulk of hot water acidulated with tartaric acid, and then poured into the dye-bath, which consists of cold water slightly acidulated: when it is well mixed, the silk is to be worked in till it is of the required shade. If a bluer shade is required, a little sulphindigotic acid may be added to the dye-bath, or the silk may previously be dyed blue with prussian blue or otherwise, and then worked in the dye-bath above mentioned. The same method serves for dyeing silk with violine or roseine.

To dye wool with aniline-purple, the dye-bath is composed of nothing but a dilute aqueous solution of the colouring matter kept at 50° or 60° C. (122° or 140° F.). Acids should be avoided, or only a very small quantity used, as they injure the colour. The same method is applicable to the dyeing of wool with fuchsine, violine, roseine, and chinoline colours.

To dye cotton with aniline purple, so as to resist the action of soap and of light, the process has to be modified, so as to form on the cotton fibre an insoluble compound of the colouring matter with tannin and a metallic base.

To effect this, the cotton has to be soaked in a decoction of sumach, galls, or any other substance rich in tannin, for an hour or two, and then passed into a weak solution of stannate of sodium, and worked in it for about an hour; it is then wrung out, turned in a dilute acid liquor, and then rinsed in water. Cotton thus prepared is of a pale yellow colour, and has a remarkable power of combining with aniline purple. The above process may be modified, as for example, the stannate of sodium may be applied to the cotton before the tannin, and alum may also be used in the place of stannate of sodium. To dye this prepared cotton with aniline-purple, it is only necessary to work it in an acidulated solution of the colouring matter; when thus prepared, the cotton will absorb all the colouring matter of the dye-bath, leaving the water perfectly colourless. It has been found that cotton thus prepared can be dyed with any colouring matter that forms an insoluble compound with tannin. It is therefore used for dyeing with roseine, violine, fuchsine, and chinoline colours.

Cotton may also be dyed a very good and fast colour by mordanting it with a basic lead-salt, and then working it in a hot solution of soap to which aniline-purple has been added.

Oiled cotton, such as is used for dyeing with madder, is also used in dyeing these colours. Cotton simply oiled, and before mordanted with alum and galls, absorbs coal-tar colouring matters with great avidity, producing very fine shades. Oiled



cotton mordanted with alum and galls also combines rapidly with these colouring matters: but as the colour of the prepared cotton is generally rather yellow, it interferes sometimes with the beauty of the result.

Cotton is sometimes washed with albumin, which is coagulated by the action of steam, and the albumin, which covers the cotton, dyed in the usual manner.

Violine, roseine, fuchsine, and also the chinoline colours, combine with unmordanted vegetable fibres as well as aniline-purple.

*Printing of Calico with Aniline-purple and other Coal-tar Colours.*—The process generally employed for printing with these colouring matters is simply to mix them with albumin or lactarin, print this mixture on the fabric, and then to coagulate the albumin or lactarin by the agency of steam.

Another method is to print tannin upon the fabric previously prepared with stannate of sodium, and then dye it in a hot dilute acid solution of the colouring matter; by this means the parts of the fabric which are covered with tannin are dyed a deep colour, but the other parts are only slightly coloured. These are cleared by well-known processes. This method of applying these colouring matters is also modified by printing a compound of the colouring matter required and tannin on the prepared cloth, instead of the tannin only, and then steaming the goods.

*Violine.*—This dye-stuff, the solutions of which have a colour resembling that of the field violet, was first obtained by Dr. D. Price. It is produced by oxidising aniline with sulphuric acid and peroxide of lead. It is even less soluble in water than aniline-purple, very soluble in alcohol. Its colour is destroyed by reducing agents, but restored on exposure to the air. The methods of dyeing with it are the same as for aniline-purple.

#### *Colours intermediate between Blue and Yellow: GREENS.*

Green dyes are, for the most part, produced by the combination of yellow and blue applied either together or separately. For the production of a good green tint, it is essential that both of the primary colours be quite pure, any admixture of red in either of them causing the green to appear dull. For dyeing green with a single bath, the stuff or fibre is sometimes mordanted with alum and then dipped into a bath of *fustic* mixed with *indigo-carmin*. When two baths are used, the stuff is first dyed blue, then well washed and boiled for three hours in a bath of *fustic* mordanted with alum and cream of tartar, mixed with a small quantity of Saxony blue (a solution of 1 pt. indigo in 6 pts. sulphuric acid). If it be then dipped into a logwood-bath, it acquires the tint called by the French, *vert-dragon*. *Saxony green*, which is brighter, is produced by dipping the piece into a second bath of *fustic* of greater concentration.

A very beautiful green colour called *Vert-Venus*, *Vert-Azof*, or *Vert-Lumière*, is produced on silk by a dye imported from China, called *Chinese green* or *Lo-Kao*; silks thus dyed are especially admired for the beautiful green shades they assume in artificial light. Very large quantities of this dye were imported in 1853 by Messrs. Guinon of Lyons. More recently, however, M. Charvin, of Lyons, has obtained the same dye from the common buckthorn (*Rhamnus catharticus*). It is remarkable for being capable of producing with proper reagents all the colours of the spectrum. Its use is, however, greatly restricted by its want of stability. Moreover, Messrs. Guinon, Marnas, and Bonnet, have found that very fine greens, which likewise maintain their colour in artificial light, may be produced at less cost by first dyeing the silk in prussian blue, and then in an acidulated bath of picric acid.

*Chrome-greens* consisting of hydrated oxide of chromium are now much used as pigments in calico-printing: for their preparation see vol. i. p. 950. They likewise maintain their colour in artificial light.

*Aniline-green, or Emeraldine.*—Aniline treated with hydrochloric acid and chlorate of potassium, or a salt of aniline treated with sesquichloride of iron, yields a green compound, the existence of which has long been known to chemists. All attempts to dye silk or wool with it have hitherto failed; but it may be produced on cotton fabrics by printing with acid hydrochlorate of aniline on a fabric prepared with chlorate of potassium. A beautiful bright green then gradually appears, and only requires to be washed. If the green fabric is passed through a solution of acid chromate of potassium, this colour is transformed into a dark indigo-blue, called *azurine*. (Calvert.)

#### *Colours composed of Red, Blue, and Yellow: BROWNS, GREYS, AND BLACKS.*

*Bronze* is produced on wool by immersion in a bath of weld, *fustic*, alum, and tartar, in which it is boiled for three hours; it is then left in a cellar for six days, washed, dipped in a bath of weld and madder, again washed and dipped in a blue bath.

For *olive*, the wool is first dyed blue, then boiled for four hours in a bath of alum, sumach, *fustic*, soot, and logwood, then taken out and redipped after addition of a small quantity of coppers. Similar processes yield *myrtle-green*, *roseada*, and other shades in which yellow is the predominating colour.

**Maroon**, in which red predominates, is obtained by boiling the stuff for three hours in a bath of weld and fustic mordanted with alum and tartar, then leaving it in the cellar for a week, washing, boiling it for a short time in a madder-bath, and lastly dipping it in a blue-bath. To obtain a darker colour, the stuff, after leaving the madder-bath, is boiled for two hours with logwood, sumach, and copperas. Similar processes are adopted for *cinnamon* and other *browns*.

**Brown Maroon** is produced by dipping the stuff for three hours in a bath of gall-nuts, sandal-wood, Brazil-wood, and madder, then adding logwood and copperas.

**Black** is produced by a mixture of indigo, various yellow dyes, and the tannin of gall-nuts or sumach, sulphates and acetates of iron and copper, cream of tartar, &c.

The black called in France *noir de sedan*, which is one of the finest and most durable, is given to wool by first dyeing it blue with indigo, then, after careful washing, dipping it for three hours in a bath of sumach and logwood, at 80° or 90° C.; then taking it out, adding to the bath 335 grammes of protosulphate of iron for each metre of stuff, redipping for an hour at 38° C., and repeating this process three times. A very fine black is likewise obtained by dyeing the wool with logwood and iron, and then dipping it in a weak solution of bichromate of potash at 40° or 50° C.

Silk is dyed black with protosalts of iron and the tannin of gall-nuts, or, more cheaply, of chestnuts. The silk is first dipped in the tannin-bath, whence it issues with a colour of nankeen yellow, then washed, and dipped in a bath of protosulphate of iron at 90° C. Pyrolignite of iron is likewise used, and iron filings and sulphate of copper are added to the bath, together with a small quantity of basic acetate of lead, to take up the sulphuric acid set free by the decomposition of the ferrous and cupric sulphates. Gum and dextrin are likewise added to give the liquid the requisite consistence. The silk, as it issues from the bath, has a rusty colour, which, however, soon turns black on exposure to the air.

Cotton and linen may be dyed black in the same manner as wool. A very black dye is also produced by dipping them first in a bath of galls and logwood, then in pyrolignite of iron at 90° C.

**Greys** of various shades are obtained in like manner by, reducing the proportions of gall-nuts, logwood, pyrolignite, &c. An alumina mordant is generally added to give a violet tint.

A variety of *brown* and *grey* tints are also produced by the fixation on the stuff of metallic oxides, such as the oxides of iron and manganese.

**Catechu-black on silk.** The silks are passed into a solution of ferric salt, then into a hot soap-solution containing an excess of soap, whence they are passed into a slightly acid bath of yellow prussiate. When thus dyed prussian blue, they are dipped into a solution of ferric salt of specific gravity 1.15, the object of which is to give an iron mordant to the silk. They are then thoroughly washed and passed into a bath of catechu, for organzine at 203°, for tram at 172° F., the silks being worked in this bath until it is cold, so as thoroughly to saturate the iron mordant with the colouring principle of catechu, and thus produce a black. They are then wrung on the peg, and exposed to the air for 24 hours, after which they are passed into a soap solution at 50° washed thoroughly; and the organzine is then dipped into a bath of weak acetic acid, the tram into a solution of weak hydrochloric acid. Finally, the silks are passed through an emulsion of oil, well worked on the peg, and left to dry. These last operations are intended to remove, by means of the fatty matters, the harshness which the silk would otherwise possess.

Catechu is capable of yielding a great variety of colours. It contains two distinct principles, *catechu-tannic acid*, and *catechin*, the former of which yields various shades of drab, while the latter yields, with metallic salts, salmon, red, and wood colours.

For further details, see the articles **DYEING** and **CALICO-PRINTING** in *Ure's Dictionary of Arts, Manufactures, and Mines*, and in *Muspratt's Chemistry*. **PÉROZ**, *Traité théorique et pratique de l'impression des Tissus*, tomes 4, 8vo. Paris, 1846. **PELOUZE** et **FRÉMY**, *Traité de Chimie générale*, Par. 1856, tom. v. pp. 558-595. **W. H. PERKIN**, *On Colouring Matters derived from Coal-tar*, Chem. Soc. J. xiv. 230. **F. C. CALVERT**, *On Improvements and Progress in Dyeing and Calico-printing* since 1851. Manchester and London.

**DYHENYLES.** Löwig's name for the organic radicles  $C^mH^{m-2}$ .

**DYOTRITYLES.** Löwig's name for the radicles  $C^mH^{m+1}$ .

**DYOXYLITE.** Syn. with **LANARKITE**.

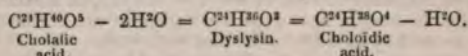
**DYSCALITE.** Syn. with **OKENITE**.

**DYSKOLITE.** Syn. with **SAUSSURITE**.



**DYSLUTE.** (Zn;Fe;Mn) (Al<sup>3</sup>,Fe<sup>2</sup>)O<sup>3</sup>.—A variety of spinel, occurring imbedded in the limestone of New Jersey. It forms octahedral crystals of a yellowish and greyish brown colour, glassy lustre, opaque. Hardness = 4·5; specific gravity = 4·55. With borax before the blowpipe, it melts to a dark garnet-red glass. (Thomson, Rammelsberg.) See SPINEL.

**DYSLYSIN.** C<sup>21</sup>H<sup>36</sup>O<sup>3</sup>. (Berzelius, Ann. Ch. Pharm. xxxiii. 139; xliii. 1.—Theyer and Schlosser, *ibid.* l. 235.—Strecker, *ibid.* lvii. 22.)—A product of the decomposition of choloïdic or cholalic acid, produced when either of these acids is heated to 300° C., or treated for some time with hydrochloric or dilute sulphuric acid



The best mode of preparing it is to boil ox-bile freed from fats and colouring matters with hydrochloric acid for 12 to 24 hours; wash the hard, friable, resinous mass which separates, with water; then boil it repeatedly with alcohol to remove admixed choloïdic acid; dissolve the residue in ether; and either evaporate the ether, which then leaves the dyslysin as a yellowish or brownish mass, or, better, precipitate the ethereal solution with alcohol, which throws it down with less colour.

Dyslysin is an amorphous substance, doubtless colourless when quite pure, but generally yellowish; melts when heated above 140° C. It is insoluble in water, acids, potash-ley, and alcohol (hence the name), but soluble in ether. Alcoholic potash converts it into choloïdic acid.

**DYSLYTE.** See EULYTE.

**DYSLYTITE.** A brown-black powder, obtained as a residue from many masses of meteoric iron when they are dissolved in hydrochloric acid. It amounts to between 0·25 and 2·25 per cent. of the entire mass, and is supposed to be a phosphide of iron, nickel, and magnesium. (Shepard, Sill. Am. J. [2] ii. 380.)

**DYSNITE, or DYSSNITE.** Syn. with RHODONITE.

**DYSODIL.** *Houille papyracée, Terre bitumineuse feuilletée, Terre folieuse bitumineuse de Melilli. Stinkkohle, blätterige Stinkerde.* A soft, finely laminated substance, occurring at Melilli in Sicily, of greenish and yellowish grey colour, and specific gravity 1·14 to 1·25. It burns with flame and an unpleasant odour, leaving a friable skeleton (Handw. d. Chem. 2<sup>e</sup>. Aufl. ii. [3] 535).

**DYSTOMITE.** Syn. with DATHOLITE.

**DYSINTRIBITE.** (Shepard, Sill. Am. J. [2] xii. 209.—Smith and Brush, *ibid.* xvi. 50.)—A rock occurring at Diana and other places in St. Lawrence County, New York. It is massive, slaty, and tough, and has the aspect of serpentine. Hardness = 3 to 3·5; specific gravity 2·76 to 2·81. Colour, green, yellow, and grey, sometimes mottled with red. Its composition varies widely, but it consists mainly of silica and alumina, with water and several protoxides in variable proportions; so that it must be regarded as a mixture. The following analyses are by Smith and Brush:—

SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	CaO	MgO	K <sup>2</sup> O	Na <sup>2</sup> O	H <sup>2</sup> O	Mn <sup>2</sup> O
44·80	34·	3·01	0·66	0·42	6·87	3·60	5·38	0·30 = 99·94
46·70	31·01	3·69	trace	0·50	11·68	trace	5·30	. . = 98·88
44·94	25·05	3·33	8·44	6·86	5·80	trace	6·15	. . = 100·57

Before the blowpipe it splits into thin splinters, and melts to a white mass, having the aspect of porcelain.

## E

**EARTHS.** This name is applied to the oxides of the metals, barium, strontium, calcium, magnesium, glucinum, aluminium, zirconium, yttrium, and thorium. The earlier chemists distinguished lime and magnesia, by the appellation of *Terræ absorbentes*, from the *earths* in a more limited sense; to these *absorbent* or *alkaline* earths, baryta, discovered in 1774 by Scheele, and strontia, discovered later, were afterwards added. Baryta, strontia, and lime, being soluble in water, and possessing strong alkaline and caustic properties, are sometimes designated *earthy alkalis*, e.g. by Gmelin in his Handbook; but the term *alkaline earths* is more generally adopted. Magnesia is usually classed among the earths proper. Silica was formerly numbered among the earths; but it is now regarded as an acid (or rather anhydride).



**EARTHY COBALT.**  
**EARTHY MANGANESE.** } See WAD.

**EAU DE COLOGNE.** *Kölnisches Wasser.*—A perfume consisting of a solution of various essential oils in alcohol. Numerous recipes have been given for its preparation. One of the best, according to Förster, is to dissolve in 6 quarts of spirit of 82 per cent. Tralles, the following mixture of oils: *Oil of orange, bergamot, lemon, limette (Citrus Lumia), essence de petits grains*, each 1 oz.; *oleum de Cedro, de Cedrat, essence de Portugal, de Neroli*, each  $\frac{1}{2}$  oz.; oil of rosemary,  $\frac{1}{2}$  oz.; oil of thyme,  $\frac{1}{8}$  oz. (Handw. d. Chem. iv. 428; see also *Ure's Dictionary of Arts, Manufactures, and Mines*, art. PERFUMERY, iii. 428.)

**EAU DE JAVELLE.** A solution of hypochlorite of sodium. (See HYPOCHLORITES.)

**EAU DE LUCE.** *Aqua Lucis.*—A milky mixture of rectified oil of amber with alcohol and ammonia.

**EBLANIN.** Syn. with PYROXANTHIN.

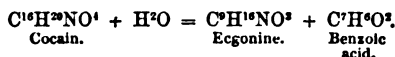
**EBONITE.** Caoutchouc hardened by kneading or rolling with half its weight of sulphur. (See CAOUTCHOUC, i. 740.)

**EBONY.** The black heart-wood of *Diospyros Ebenum*, a tree of the styraceous order, indigenous in Ceylon, Madagascar, the Mauritius, and many other tropical countries. It is very hard, heavier than water, and takes a fine polish. It has a biting taste, and gives off an aromatic odour when burnt. According to Petersen and Schödler, it contains, when dried at 100° C., 49.8 per cent. carbon, 5.3 hydrogen, and 44.9 oxygen.

**EBULLIOSCOPE.** *Ebullition Alcoholometer.*—An instrument for determining the strength of hydrated alcohol by its boiling point. (See ALCOHOL, i. 95; also *Ure's Dictionary of Arts, Manufactures, and Mines*, ii. 72.)

**EBULLITION.** See HEAT.

**ECGONINE.** *Ekgonine* (from *Ekrynos*, offshoot).  $C^9H^{16}NO^2$ .—A base obtained by the decomposition of cocain under the influence of hydrochloric acid:



It is most readily obtained by heating cocain with hydrochloric acid to 100° C. in a sealed tube. It is soluble in water. Its platinum-salt crystallises in orange-yellow prisms. (Wöhler, Ann. Ch. Pharm. cxxi. 372.)

**ECHINITES.** Fossil radiate animals found in the chalk.

**ECLOGITE.** *Smaragdite-rock, Omphazite-rock.*—A crystallo-granular rock consisting essentially of red garnet and green smaragdite, sometimes also containing kyanite and white mica.

**EDDOES.** (*Arum esculentum*).—A plant cultivated for food in most tropical climates. According to T. J. Herapath (Chem. Soc. Qu. J. iii. 196), the fresh roots yield 1.647 per cent. ash, containing in 100 pts.:

Matter soluble in water:

K <sup>2</sup> O	NaCl	SO <sup>3</sup>	CO <sup>2</sup>	P <sup>2</sup> O <sup>5</sup>	Total.
38.9	7.0	3.3	10.4	4.1	63.7

Matter insoluble in water:

Ca <sup>2</sup> O	Mg <sup>2</sup> O	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	SO <sup>3</sup>	SiO <sup>2</sup>	CO <sup>2</sup>	P <sup>2</sup> O <sup>5</sup>	
15.7	trace	trace	1.0	1.1	5.2	3.5	9.8	36.3
								100.0

From these results Herapath concludes that eddoes exhausts the soil of phosphoric acid and alkalis more than the Spanish potato or batatas (i. 520), but less than the common potato.

**EDELFORSITE.** *Aedelforsite.*—A silicate of calcium,  $2Ca^2O.3SiO^2$ , or  $Ca^2Si^3O^8$ , found at Aedelfors in Småland, Sweden, Cziklowa in the Bannat, and Gjelleback in Norway. It is massive, fibrous or feathery, white or greyish, with vitreous lustre and transparent. Specific gravity = 2.58. Hardness = 5.5. Melts to a clear glass before the blowpipe. (Hisinger, Kongl. Vetensk. Acad. Handl. 1823, p. 177; 1838, p. 191.)

The same name is given by Retzius (*Dissert. de Trem. Norweg. et zeolo rubro*, Aedelfors, Lundæ, 1818) to the red zeolite of Aedelfors, which occurs there in fibrous aggregations, white, light grey, or reddish, translucent on the edges, and with a vitreous lustre. Specific gravity = 2.6. Hardness = 6. According to Retzius, it contains 60.28 per cent.  $\text{SiO}_2$ , 15.42  $\text{Al}_2\text{O}_3$ , 8.18  $\text{CaO}$ , 4.16  $\text{Fe}_2\text{O}_3$ , 0.42  $\text{MgO}$  and  $\text{Mn}_2\text{O}_3$ , and 11.07 water. A similar mineral from Fahlun in Sweden was found by Hisinger to contain 60.0  $\text{SiO}_2$ , 15.6  $\text{Al}_2\text{O}_3$ , 1.8  $\text{Fe}_2\text{O}_3$ , 8.0  $\text{CaO}$ , and 11.6 water (= 97.0), while he obtained from the Aedelfors zeolite 53.76  $\text{SiO}_2$ , 18.17  $\text{Al}_2\text{O}_3$ , 4.02  $\text{Fe}_2\text{O}_3$ , 10.90  $\text{CaO}$ , and 11.23  $\text{H}_2\text{O}$  (= 98.38). (Dana, ii. 307.)

**EDELITE.** Prehnite from Aedelfors in Sweden.

**EDENITE.** Grammatite from Edenville, Orange County, New York.

**EDINGTONITE.** A mineral occurring on the Kilpatrick Hills, near Glasgow, in small crystals belonging to the dimetric or quadratic system. The crystals are square prisms, acuminate with the faces of a quadratic octahedron. Colour greyish white. Hardness = 4.0 to 4.5. Specific gravity 2.694. According to Heddle's analysis (Phil. Mag. [4] ix. 179), it contains 36.98  $\text{SiO}_2$ , 22.63  $\text{Al}_2\text{O}_3$ , 26.84  $\text{BaO}$ , 12.46 water, with traces of soda and lime (total 98.91), whence may be deduced the formula  $3\text{BaO} \cdot 2\text{SiO}_2 + 4(\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) + 12\text{H}_2\text{O}$ , which is equivalent to  $(\text{Ba}^{60}\text{Al}^{74}\text{H}^{10})\text{Si}^{100} + 7\text{aq.}$ , and reducible to  $\text{R}^+\text{SiO}_4 + 7\text{aq.}$ , the formula of an orthosilicate.

**EDUCT.** This term is applied to a body separated by the decomposition of another in which it previously existed as such, in contradistinction to product, which denotes a compound not previously existing, but formed during the decomposition. The volatile oil of lemon-peel is an educt, because it pre-exists in the peel; but bitter almond oil is a product, because it does not exist ready formed in bitter almonds, but is produced by the action of emulsin and water on amygdalin. In many cases, however, the same substance may be regarded as an educt or as a product, according to the view which is taken of the constitution of the body from which it is derived. Thus the lime and carbonic anhydride obtained by heating chalk to redness, are educts, if the chalk be regarded as  $\text{Ca}^{100}\text{CO}_2$ , products if it be regarded as  $\text{Ca}^{50}\text{CO}_2$ , or  $(\text{CO})^{50} \cdot \text{Ca}^{50}\text{O}$ , &c. Similarly the ammonia evolved by heating sal-ammoniac with lime is an educt, if that salt is composed of  $\text{NH}_4\text{HCl}$ , but a product if its composition is that expressed by the formula  $\text{NH}_4\text{Cl}$ . Even the elementary bodies, as evolved from their compounds, may be regarded as products, if, as explained in the article CHEMICAL AFFINITY (i. 858), we suppose a molecule of a free element to be formed by the union of two elementary atoms in opposite polar states; as for example, when hydrogen

is evolved by the action of hydrochloric acid on hydride of copper:  $\text{Cu}^{+}\text{H}^{-} + \text{H}^{+}\text{Cl}^{-} = \text{Cu}^{+}\text{Cl}^{-} + \text{H}^{+}\text{H}^{-}$ , or when sulphur is precipitated by the mutual action of sulphurous anhydride and sulphydric acid:  $2\text{H}^{+}\text{S}^{-} + \text{SO}^{+} = 2\text{H}^{+}\text{O}^{-} + \text{S}^{+}\text{S}^{-}$ .

**EDULCORATION.** A term applied to washing, or lixiviation, in cases when the soluble matter is rejected as worthless, and the insoluble residue is the material required.

**EDWARDSITE.** See MONAZITE.

**EFFERVESCENCE** is the commotion produced in liquids by some part of the mass suddenly taking the gaseous form and escaping in numerous bubbles.

**EFFLORESCENCE.** This term is applied to two or three different phenomena, characterised by the formation of a loose pulverulent deposit on the surface of a solid body.

1. Crystallised salts are said to effloresce when they lose their water of crystallisation and fall to powder: e. g. neutral carbonate of sodium,  $\text{Na}_2\text{CO}_3 + 5\text{aq.}$

2. The formation of a pulverulent crystalline deposit on the surface of a porous body, in consequence of the crystallisation of a salt existing in solution within its pores, or formed from materials existing therein, is also called efflorescence: e. g. the crystallisation of nitrate of potassium on the surface of the earth or in caves, as in India, or on saltpetre plantations,—of sulphate and carbonate of sodium on walls,—of alum on alum-slate,—of ferrous sulphate on iron pyrites, &c. In all these cases, the solution of the salt is drawn by capillary action to the surface of the solid body, and there crystallises in consequence of the evaporation of the water.

3. The term efflorescence is likewise applied to the effect which sometimes takes place when a saline solution is left to evaporate slowly in an open vessel. The solid salt separates in dendritic crystals just where the surface of the liquid touches the side of the vessel, and the solution, rising by capillarity between these crystals, forms a

fresh crystallisation just above the first layer; and this process is continually repeated till the crystallisation thus formed extends over the edge of the vessel, and sometimes down to the table on which it stands. Sal-ammoniac and other ammonia-salts often effloresce in this manner. The effect may be prevented to a certain extent by greasing the edge of the vessel, or, better, by quickly boiling the solution, or evaporating it by heat from above.

**EGERAN.** Syn. with IDOCRASE.

**EGG.** (Prout, Phil. Trans. 1822, p. 377.—Prévost and Dumas, Ann. d.Sc. nat. iv. 47.—Prévost and Morin, *Lehmann's Zoochemie*, Heidelberg, 1858, p. 693.—Baudrimont and St. Ange, Compt. rend. xvii. 1343.—Gobley, Compt. rend. xxi. 766.—J. Phys. Chim. [3] xi. 409; xii. 513.—Valenciennes and Frémy, J. Pharm. [3] xxvi. 5, 321, 416; *Traité de Chimie générale par Pelouze et Frémy*, 2<sup>nd</sup> Ed. 1857, vi. 227.—Lehmann, *Lehrbuch d. physiol. Chemie*, translated by Dr. Day, ii. 353; iii. 439; also in *Gmelin's Handbuch*, viii. 282, 646, 667, 668, and 693.—Handw. d. Chem. 2<sup>nd</sup> Aufl. ii. [3] 342, 554, 652.)

The eggs of birds consist of four parts, viz. 1. The shell, which is a hard calcareous envelope; 2. A thin membrane, called the *membrana putaminis*, which lines the shell; 3. The white, or albumen, which is a colourless liquid enclosed in large cells formed of a thin membrane; and 4. The yolk or vitellum surrounded by the albumen, and likewise enclosed in a membrane, which is connected with that which forms the cells of the albumen by two knotted ligaments called *chalazæ*.

The shell consists mainly of carbonate of calcium, with smaller quantities of phosphate of calcium and animal matter. In the egg-shells of the domestic fowl, Vauquelin and Proust found,

	Vauquelin.	Proust.
Carbonate of calcium . . . . .	89.6	91
Phosphate of calcium, with a little phosphate of magnesium . . . . .	5.7	7
Animal matter containing sulphur . . . . .	4.7	2
	100.0	100

The egg-shell of the ostrich contains, according to Wicke, 3.28 p. c. organic matter and 97.41 carbonate of calcium.

The lining membrane of the shell of poultry eggs contains, according to Scherer, 50.7 p. c. carbon, 6.6 hydrogen, 16.8 nitrogen, and 26.0 oxygen and sulphur. When incinerated, it leaves a small quantity of ash consisting chiefly of phosphate of calcium.

The white or albumen of the egg is not a mere solution of albumin or albuminate of sodium in water. When examined by the microscope, it exhibits, besides the *chalazæ* and the amorphous cellular membranes, a number of small bodies with three projecting points, or aggregates of small needles, consisting of fat. The cellular membrane is that which gives the gelatinous consistence to white of egg. When the white is beaten up with water, and the intimate mixture thus formed is diluted with a large quantity of water, the *chalazæ* and membranes separate as a flocculent sediment.

Lehmann found in white of egg, in addition to albumin, a small quantity of fat, glucose, extractive matter, mineral salts, and free gases. Nicklès found a trace of fluorine. In the fresh white of poultry eggs, Lehmann found carbonates in variable quantity, depending perhaps on the time for which the eggs had been exposed to the air. The quantity of water in the albumen varies from 82 to 88 p. c.; the quantity of albumin, mostly in combination with soda, is about 12.5 p. c. of the fresh albumen; that of the extractive matters is 3.14 p. c. of the solid residue. The proportion of inorganic salts is 0.64 to 0.68 (Lehmann), 0.65 (Poleck). The dried residue of the albumen yields 3.042 p. c. fusible ash (Lehmann). In the dried albumen of poultry eggs, Lehmann found, as an average of numerous determinations, 0.6 p. c. fermentable sugar. G. Meissner found a much larger quantity, viz. 8 p. c. of the dried residue. In 100 pts. of the ash of the albumen of poultry eggs, Poleck found 25.67 KCl, 8.57 NaCl, 5.43 K<sub>2</sub>O, 12.49 Na<sub>2</sub>O, 6.25 Ca<sub>2</sub>O, 7.03 Mg<sub>2</sub>O, 2.09 Fe<sub>2</sub>O<sub>3</sub>, 16.28 P<sub>2</sub>O<sub>5</sub>, 0.84 SO<sub>3</sub>, 9.01 CO<sub>2</sub>, and 7.06 SiO<sub>2</sub>. The chlorides and other soluble salts form the larger portion of this ash, whereas in the ash of the yolk, the insoluble salts predominate.

The yolk of birds' eggs forms a thick, viscid, slightly translucent, yellow liquid, destitute of odour, but having a faint peculiar taste: when mixed with water, it forms a white emulsion. It blues reddened litmus paper, solidifies to a friable mass when boiled, is coagulated by cold alcohol, and gives up to ether a reddish-yellow fat. When examined by the microscope, it is found to consist of a semifluid mass of very fine granules, amongst which there swim variously sized yolk-corpuscles and fat globules.

The yolk-corpuscles consist mainly of fat and pigment; the fine granules, according



to Lehmann, of casein containing but a small quantity of alkali; the fluid of the yolk consists of albumin poor in alkali, in a state of actual solution. The substance formerly called vitellin is now known to be a mixture of casein and albumin.

The fat of the yolk appears to consist chiefly of olein and palmitin; it also contains cholesterin or a very similar body, and according to Gobley, cerebrin and lecithin (*q. v.*) The colouring matters of the yolk have not been accurately investigated: it is merely known that they consist of a red and a yellow pigment, one or the other of which is albuminous.

In 1000 pts. of the yolk of the egg of the domestic fowl, Gobley found 514.90 water, 157.60 vitellin, 304.70 fat (consisting of 213.00 palmitin and olein, 4.40 cholesterin, 84.30 lecithin and 3.00 cerebrin), 4.00 alcoholic extract, 5.50 colouring matter, 0.30 chloride of ammonium, 2.80 alkaline chlorides and sulphates, 10.20 earthy phosphates, with a trace of oxide of iron.

Among the constituents of the ash, the potassium-salts and phosphates occupy the chief place, the chlorides and the sodium-salts being present in small quantity only. Poleck found in 100 pts. of the ash of the yolk of hens' eggs, 5.94 potash, 4.82 soda, 15.79 lime, 2.36 magnesia, 1.85 ferric oxide, 68.26 phosphoric anhydride, and 0.92 silica (= 99.94).

*Changes of the egg during incubation.*—From observations on the eggs of the domestic fowl, Prout deduced the following conclusions:

1. The relative weights of the several parts of the egg vary considerably. Ten eggs gave on the average, in 1000 pts.; shell and lining membrane 106.9 pts., white 604.2, yolk 288.9. The membrane weighs about  $2\frac{1}{2}$  pts. per thousand of the entire egg.—2. The egg loses during incubation about  $\frac{1}{3}$  of its weight, which is about eight times as much as it would lose in the same time if left to itself.—3. At the commencement of incubation, the yolk gives up oil to the white, whereby the white is altered and becomes like the casein of milk, the yolk at the same time taking up water and salts.—4. At a later stage, the water and salts leave the yolk, which gradually resumes its original volume. In the last week of incubation, it diminishes still further in bulk, and gives up the greater part of its phosphorus, which is used in the formation of bone, uniting as phosphoric acid with lime, which is not originally contained in the fluids of the egg, but appears to be derived from the shell.

The results obtained by Prévost and Dumas are as follows: The contents of the unincubated egg were found to consist of 10.72 per cent. fat, 16.58 substance free from fat (8.19 in the white and 8.36 in the yolk) and 72.55 per cent. water. After seven days' incubation, the inner part of the egg consisted of 9.32 per cent. ether-extract, 13.94 substance free from fat (with 8 per cent. albumin), and 76.74 water. Of substance free from fat the white contained 34.9 per cent., the thick yolk 16.5, the fluid yolk 4.4, the membranes of the white 7.7, the amniotic liquid 1.3 per cent. The fat and solid substance had therefore diminished during incubation, but the amount of water was relatively increased after fourteen days' incubation, the lining membrane of the shell, the interior of the fœtus, and in one instance also, the amniotic liquid exhibited an acid reaction. 100 pts. of the interior of the egg consisted of 9.46 ether-extract, 16.09 dry matter with 7.7 albumin, and 74.43 water. The white contained 3.3 per cent. dry matter free from fat; the yolk 19.3; the membranes 9.1; the fœtus 7.2; the amnios 1.4 per cent. After twenty-one days' incubation, the interior of the egg consisted of 5.68 per cent. fat, 15.44 dry substance free from fat ( $\frac{1}{3}$  of which was yolk,  $\frac{1}{3}$  yolk-membrane and  $\frac{2}{3}$  fœtus), and 78.88 per cent. water. The yolk then contained 29.0 per cent. the yolk membrane 20.6, the fœtus 14.6 per cent. dry matter free from fat.

The weight of the shell remained nearly constant. The fat of the egg before incubation had a uniform yellow colour; on the seventh day the thick yolk yielded to ether a yellow oil; the liquid yolk a yellow, later a colourless fat. The membranes and amnios yielded a thick white fat, the fœtus a white fat like hog's lard. On the fourteenth day, the yolk-oil was yellow and thick; that of the fœtus reddish and solid. On the twenty-first day, the yolk-fat was thick and pale yellow; that of the membranes dark yellow and partially solid: the fœtus yielded at first a solid yellow, afterwards a soft, white fat.

Respecting the mineral constituents of eggs, Prévost and Morin have obtained the following results:

Eggs before incubation contained;

	Dry substance free from fat.	Ash.	Insoluble phosphates.	Soluble salts.
In the white . . .	15.090	0.85	0.13	0.68
In the yolk . . .	15.166	0.90	0.90	
	30.256	1.75	1.03	0.68

After twenty-one days incubation :

	Dry substance free from fat.	Ash.	Insoluble phosphates.	Soluble salts.
In the yolk . . . . .	5.51	0.150	0.145	0.005
„ yolk-membrane . . . . .	4.80	0.205	0.205	
„ putamen, chorion and amnios. } . . . . .	0.42	0.040	0.015	0.025
„ fœtus . . . . .	16.87	1.825	1.059	0.730
	27.60	2.220	1.424	0.760

The loss of weight of the egg during incubation was found by Prévost and Morin (contrary to the observations of Prout, p. 364) to be the same in a given time as that of the egg when left to itself, so that it appears to arise from simple drying. Unimpregnated eggs do not putrefy during incubation, their contents retain their original consistence, but the yolk becomes darker.

It has long been known that non-incubated eggs respire, giving off water and carbonic acid and absorbing oxygen, so that the air confined at the broad end of the egg is richer in oxygen than the external air. From the investigations of Baudrimont and St. Ange, as well as from those of Viborg and Schwann, it appears that this process of respiration, in other words, the interchange of gas through the shell, is accelerated during incubation, and is moreover necessary to the process of development, inasmuch as eggs enclosed in an atmosphere of hydrogen or carbonic anhydride quickly die.

*Eggs of Fishes.*—The eggs of fishes, and likewise those of reptiles, insects, mollusca, &c., do not contain an albuminous investment like that of birds' eggs, but consist merely of a fluid corresponding to the yolk, and enclosed in a membrane, which is itself enclosed in a shell.

The yolk, or vitellum, of the eggs of cartilaginous fishes consists of an albuminous liquid, holding in solution certain mineral salts, chiefly chlorides and phosphates, and in suspension, white grains or plates, consisting of ichthin, the form of which is regular and constant in each species, but differs in different species. According to Radlkofer, they are crystalline and double-refracting. These grains are mixed with a small quantity of phosphoretted fat, which is soluble in ether and alcohol, forms a kind of mucilage with water, and exhibits some analogy to the oleophosphoric acid of the brain. (Valenciennes and Frémy.)

The roe of the sturgeon is salted and sold as *caviare*. John found in 100 pts. of it, 6.2 fluid albumin, 4.3 butyraceous fat, 6.7 common salt, 0.5 phosphate of calcium with a little iron, 24.3 coagulated albumin, and 58 water.

The eggs of bony fishes also contain grains or plates similar to those in the yolk of cartilaginous fishes, but consisting of three substances insoluble in water, viz. ichthin, ichthidin, and ichthulin. The albumin of fishes' eggs appears to differ from that of birds' eggs; in fact, that of certain fishes dissolves in hydrochloric acid without coloration, and begins to coagulate at 45° C., whereas the albumin of birds' eggs dissolves in hydrochloric acid with deep violet-blue colour, and does not coagulate below 60° C.

The fluids of the eggs of bony fishes undergo a change of composition during their sojourn in the oviduct. While still attached to the ovary, they contain only traces of albumin, but those in the oviduct contain a considerable quantity of it. The eggs of the *carp* in an early stage of development contain ichthidin and ichthulin; when fully developed, they no longer contain ichthidin, the ichthulin gradually disappears, and when they have become quite transparent, they contain nothing but a strongly albuminous liquid, holding phosphoretted fat in suspension. (Valenciennes and Frémy.)

According to Gobley (J. Phys. Chim. [3] xi. 409; xii. 513), carps' eggs exhibit in their composition a certain degree of similarity to hens' eggs. They appear to be deficient in the alkaline albumin which surrounds the yolk of the fowl's egg, but they contain an albuminous substance, paravitellin, agreeing in composition and properties with vitellin, and a fat, which, like that of the yolk of poultry eggs, is composed of a fixed oil and a tenacious infusible substance. The oil, which is present in small quantity only, consists of olein and palmitin; the tenacious substance is a mixture of several compounds, including cholesterin, lecithin, and cerebrin, the second of which contains phosphorus. Carps' eggs boiled with water yield, according to Gobley, an acid liquid, which becomes more acid on addition of alcohol. The colouring matter of carps' eggs appears to be of two kinds, like that of poultry eggs, a red ferruginous substance, like the colouring matter of blood, and a yellow substance. Gobley gives the mean percentage composition of the eggs, as follows:—64.08 water, 14.06 paravitellin, 2.57 olein and palmitin, 0.26 cholesterin, 3.04 lecithin, 0.20 cerebrin, 0.04 chloride of ammonium, 0.45 chlorides of potassium and sodium, 0.04 sulphate and phosphate of



potassium, 0.29 phosphates of magnesium and calcium, 0.39 extract of flesh, 14.53 membrane, and 0.03 colouring matter, with traces of iron, and loss.

*Eggs of Reptiles.*—The eggs of the *tortoise* are composed of a gelatinous white, small in quantity, containing but little albumin, and enclosed in the cells of the large transparent membranes. The yolk is very rich in albumin, and contains a considerable quantity of phosphoretted oil together with grains of emydin (*q. v.*).

In the egg-shell of *Emys amazonica*, L. Gmelin found 26.6 per cent. animal matter insoluble in hydrochloric acid, 10.7 animal matter soluble in that acid, 55.4 carbonate of calcium, 7.3 phosphate of calcium, and traces of magnesia.

In the egg-shell of *Alligator solerops*, not quite freed from membrane, Brummerstadt found 1.36 per cent. water, 5.99 organic matter, 91.10 carbonate of calcium, 2.33 carbonate of magnesium, and 0.54 earthy phosphates.

The eggs of the *lizard* resemble those of the *tortoise* to a certain extent; they do not contain ichthin or emydin. (Valenciennes and Frémy.)

The eggs of the common *viper* contain an albumin, like that of the ray, gelatinous, and made up of transparent elastic films containing a slightly albuminated water. The yolk contains a liquid very rich in albumin, and having a large quantity of fat floating in it, but on bringing it in contact with water, the liquid thickens more and more; and at last becomes quite gelatinous. This change of state is due to the presence of a body resembling vitellin, which is rendered insoluble by the slow action of water. (Valenciennes and Frémy.)

The gelatinous matter of the eggs of *frogs* is composed of a tissue of hyaloid membranes, containing water, absorbed after the eggs have been laid. It is modified by boiling, becoming slightly opaline, while the yolk hardens, showing that it contains albumin. The yolk is blackened by a peculiar pigment, which also colours the extremely thin vitelline membrane; the liquid of the yolk contains a very small quantity of fatty matter united in transparent drops: another substance which, under the microscope, presents the appearance of an extremely thin membrane, covered with black dots, and a large quantity of extremely small vitelline granules, insoluble in water, but soluble in acetic acid. The eggs of *tritons* exhibit the same composition; the white exterior matter is similar to that of frogs' eggs.

The eggs of *Crustaceans* do not contain ichthulin; their albumin appears to differ in some respects from that of other eggs, not coagulating below 74° C. The eggs of *crabs* and *lobsters* contain the substance which exists in the shell of the animal, and is the cause of the red colour which it assumes when boiled. In the eggs, this substance appears to be in a state of solution, and to be precipitated, on diluting the crushed eggs with water, as a green resinous substance, which is reddened even by drying in vacuo, also by the action of salts which absorb water, by the action of alcohol or ether, and lastly when rubbed with a solid body. In the reddened state, the colouring matter may easily be obtained by heating the albuminous liquid which holds it in solution, and dissolving out the colouring matter from the coagulated albumin which encloses it, by means of alcohol. (Valenciennes and Frémy.)

*Eggs of Arachnida and Insects.*—The eggs of *spiders* contain albumin, fatty matters and a large quantity of matter precipitable by water. The eggs of *ants* exhibit similar composition. (Valenciennes and Frémy.)

Reinsch found in the eggs of *Papilio Cratægi*, 2.36 per cent. shell (containing 2.14 animal matter, and 0.22 carbonate of calcium), 8.32 albumin, 8.22 fat, with traces of volatile oil, 0.88 unsaponifiable fat, 0.57 phosphate of calcium, with traces of ferric oxide, 4.65 animal substances with salts, and 75.00 water.

*Eggs of Mollusca.*—These eggs appear to differ altogether in composition from those of other animals. Thus the eggs of the *snail* do not contain a trace of fat, but are formed entirely of hyaloid membranes, enclosing a viscid, colourless liquid, which holds in solution an azotised body different from albumin, inasmuch as it does not coagulate by heat, is precipitated by acetic acid, and dissolves in hydrochloric acid, without producing a violet colour. (Valenciennes and Frémy.)

F. W. Burdach examined the eggs of *Limnæus stagnalis*, in different stages of development, with the view of ascertaining whether the quantity of fat in them increases during their development at the expense of the albuminoids. The eggs in an early stage of development were found to contain in the dry state, 4.05 per cent. mineral salts, 0.65 fat, and therefore, 95.26 albuminates; in a second experiment, 3.55 salts, 0.64 fat, and 95.81 albuminates. The fully developed eggs yielded 6.00 and 6.62 per cent. salts, 2.18 and 1.55 fat, and 91.82 albuminates. These experiments seem to show that the albuminates are partly converted into fat in the process of development. (Burdach, *De commutat. subst. protein. in adipem*, *Dissertatio*. Regiomontii Prussor. 1853.)

The following general conclusions are deduced by Valenciennes and Frémy from their researches on the eggs of different classes and orders of animals.



1. Among vertebrate animals, the eggs of birds, reptiles, and fishes exhibit differences which may be demonstrated by the most simple analysis; nevertheless, the eggs of saurians and ophidians present considerable analogy to those of birds, whereas the eggs of batrachians approach more to those of cartilaginous fishes.

2. The eggs of arachnids and insects differ altogether in composition from those of other animals.

3. The eggs of crustaceans, which are organised so as to be hatched in water, exhibit no resemblance to those of fishes or amphibious vertebrata.

4. Similar observations apply to the eggs of molluscs.

5. These differences correspond not only with classes and orders, but likewise extend to natural families, and do not stop even there; inasmuch as the eggs of cartilaginous fishes have not the same composition as those of bony fishes: moreover, a carp's egg is very different from that of a salmon, and the egg of an ophidian, an adder, for example, does not contain the same principles as that of a chelonian.

6. Eggs contain several distinct proximate principles, viz. vitellin, ichthin, ichthulin, ichthidin, and emydin, designated by the generic name of *vitelline substances*.

7. Though the composition of the proximate principles is the same in closely allied species, the form and size of the vitelline substances varies sufficiently to be recognised and assigned for each species.

8. The albuminous substances derived from the eggs of birds, reptiles, fishes and crustaceans exhibit in their chemical properties and in their point of conglomeration, differences sufficient to justify the conclusion that they constitute different proximate principles.

9. An egg undergoes changes attended with considerable modifications of its liquid constituents, at the different epochs of its formation, at the moment of its separation from the ovary, and during its sojourn in the oviduct before it is laid.

**EHLITE.** A basic phosphate (or phosphovanadate) of copper found at Ehl, near Linz on the Rhine, at Nischnei-Tagilek in the Ural, and at Libethen in Hungary (the so-called *crude Mbeikenite*), usually in botryoidal and kidney-shaped aggregates, or massive and imbedded, rarely crystallised. It cleaves in one direction, produces a verdigris-green to emerald-green streak, is translucent on the edges, has a nacreous lustre on the cleavage faces. Hardness = 1·5 to 4·0. Specific gravity = 3·8 to 4·3. Before the blowpipe it decrepitates violently, and melts easily to a black bead, which solidifies in the crystalline state. On charcoal it yields copper. Dissolves easily in hydrochloric acid and in ammonia.

According to an older analysis by Bergemann (Schw. J. liv. 305), it contains 24·93 per cent.  $P_2O_5$ , 65·99  $Cu_2O$ , and 9·08 water, agreeing approximately with the formula  $5Cu_2O.P_2O_5 + \frac{3}{2}H_2O$ , or  $2(Cu_2O.P_2O_5.2CuHO) + H_2O$  (calc. 23·94  $P_2O_5$ , 66·97  $Cu_2O$ , and 9·09 water). Analyses by R. Hermann (J. pr. Chem. xxxvii. 183), Rhodius (*ibid.* xlii. 467), and Nordenskiöld (*ibid.* lxxii. 457), lead to similar results. According to a later analysis by Bergemann (Jahresber. v. Leonhard f. Min. 1858, p. 191), the mineral likewise contains vanadium, viz. 7·34  $V_2O_5$ , 17·89  $P_2O_5$ , 64·09  $Cu_2O$ , and 8·90, which may be represented by the formula  $3Cu_2O.V_2O_5 + 6(3Cu_2O.P_2O_5 + aq.) + 3(Cu_2O.H_2O)$ , or  $Cu_2VO_3.3(2Cu_2O.P_2O_5.aq.).3CuHO$ . But it is probably a mixture, as indeed might be inferred from the great variations in its hardness and density.

**EHRENBURGITE.** An amorphous mineral occurring as a deposit in trachyte in the Siebengebirg. In the recent state it is nearly gelatinous, easily compressible, and when dried becomes lighter in colour, fissured, fine-grained, and opaque. In the dry state it adheres but little to the tongue. In water it disintegrates and resumes its original character. According to Ehrenberg, it becomes white by gentle ignition, but recovers its former colour by immersion in water. Analyses by Bischof (I.) and Schnabel (II.) show that its composition is very variable:

	SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	Mn <sup>2</sup> O	Cu <sup>2</sup> O	Mg <sup>2</sup> O	H <sup>2</sup> O	K <sup>2</sup> O, Na <sup>2</sup> O	Total.
I.	64·64	6·04	4·66	4·61	3·96	0·41	7·77	8·11	100
II.	66·77	6·77	1·65	0·86	2·76	1·30	17·11	3·78	100

According to Schnabel, water extracts from it chlorine, sulphuric acid, and magnesia; hydrochloric acid extracts iron and manganese. (Jahresber. d. Chem. 1852, p. 367.)

**EHRENBURGITE.** A massive fibrous variety of Scapolite (q. v.)

**ELAEWA.** OH<sup>2</sup>.—Syn. with NONTLENE (q. v.)

**ELÆOLITE.** A variety of nephelin, having a waxy or fatty lustre, slight translucence, and a grey, dingy blue, green, red, or brown colour. In crystalline form and composition it does not differ essentially from nephelin, but is distinguished by the greater ease with which it melts to a tumid glass. (See NEPHELIN.)

**ELÆOMETER.** A kind of hydrometer for detecting adulterations in fixed oils,

such as palm-oil, linseed-oil, &c., by their specific gravity, and partly also by their different rates of expansion by heat. The indications are not very exact.

**ELÆOPTENE.** A term applied to the more volatile portion of a natural essential oil, the other portion, which solidifies more readily, being called a stearoptene or camphor.

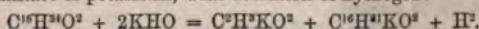
**ELÆOSACCHARUM.** *Oelzucker.*—A finely triturated mixture of sugar with a volatile oil (e. g. oil of anise, lemon, &c. *Elæosaccharum anisi, citri*, &c.). Such mixtures may be prepared by rubbing the rind of lemons, oranges, &c., or the fruits themselves, on loaf sugar, or by directly mixing the aromatic substance with the sugar, as in the preparation of vanilla.

**ELAËRIN.** The name given by Chevreul to the more fusible constituent of the grease of sheep's wool, in which it is associated with stearin. It is said to saponify with difficulty, yielding a peculiar acid, *elaëric acid*. Neither the fat nor the acid has been sufficiently examined to establish its separate identity.

**ELAÏC ACID.** Syn. with OLEIC ACID.

**ELAÏDIC ACID.**  $C^{18}H^{32}O^2$ . (Boudet, Ann. Ch. Phys. l. 391.—Laurent, *ibid.* lxx. 149.—Meyer, Ann. Ch. Pharm. xxxv. 174.—Gottlieb, *ibid.* lvii. 64.)—A solid isomeric modification of oleic acid, produced by the action of nitrous acid. It may be obtained by solidifying olive oil with vapour of nitrous acid, or with mercurous nitrate, saponifying the solid glyceride thus obtained (*elaïdin*), and decomposing it with a mineral acid. The *elaïdic acid* thus obtained is, however, always more or less contaminated with margaric acid. A better process is to treat pure oleic acid with nitrous acid. *Elaidic acid* may also be prepared by decomposing oleate of barium with a quantity of fuming nitric acid, exactly sufficient to unite with the baryta. On leaving the liquid at rest, the *elaïdic acid* rises to the surface, and may be freed from unaltered oleic acid by pressure between bibulous paper and crystallisation from alcohol.

*Elaidic acid* melts between  $44^{\circ}$  and  $45^{\circ}$  C. It dissolves readily in alcohol, and is deposited from the concentrated solution in laminae resembling benzoic acid; it likewise dissolves in ether, but not so freely. The solutions have an acid reaction. When kept for a long time at  $65^{\circ}$  C. it absorbs oxygen, acquires a disagreeable odour, liquefies, and is then no longer solidified by nitrous acid. *Elaidic acid* distils for the most part without alteration. Treated with melting potash it is converted, like oleic acid, into acetate and palmitate of potassium, with evolution of hydrogen:



The *ELAÏDATES*,  $C^{18}H^{32}MO^2$ , are isomeric with the oleates. All the neutral *elaïdates* are insoluble in water, only the alkaline salts containing excess of alkali being soluble. An excess of water decomposes them, precipitating acid salts.

*Elaidate of ammonium* crystallises in scales; it is sparingly soluble in ether. The *potassium-salt* also crystallises in scales; the *sodium-salt* in large shining leaflets. The *barium-* and *lead-salts* are white precipitates. The *silver-salt*,  $C^{18}H^{32}AgO^2$ , is a white precipitate, sparingly soluble in water, alcohol, and ether, when once dried, easily soluble when recently precipitated. It dissolves easily in warm aqueous ammonia, and is deposited in great part on cooling in small prismatic crystals.

**ELAÏDIC ETHERS.** (Laurent, Ann. Ch. Phys. xxxv. 296.—Meyer, Ann. Ch. Pharm. xxxv. 186.)—*Elaidate of Ethyl*,  $C^{18}H^{32}O^2.C^2H^5$ , is obtained by boiling 2 pts. of *elaïdic acid* with 1 pt. of sulphuric acid and 4 pts. of alcohol, boiling the mixture, with cohobation, for several hours; also by saturating an alcoholic solution of *elaïdic acid* with hydrochloric acid. It is a colourless oil, odourless in the cold, of specific gravity 0.869 at  $18^{\circ}$  C.; insoluble in water. Alcohol dissolves about  $\frac{1}{2}$  of its volume of it; ether dissolves it in all proportions. It boils a little above  $310^{\circ}$  C., and distils without alteration, according to Laurent; according to Meyer, it is decomposed by distillation. Alkalis in alcoholic solution convert it into an alkaline *elaïdate*.

*Elaidate of Methyl*,  $C^{18}H^{32}O^2.CH^3$ .—Prepared like the preceding compound. It is an oily liquid of specific gravity 0.872 at  $18^{\circ}$  C.

**ELAÏDIN.** A solid isomeric modification of olein, produced by the action of nitrous acid (or of nitric acid in contact with mercury) on olein; fuming nitric acid also solidifies olein after some time, but an excess of the acid hinders the solidification. *Elaidin*, like olein, has never been obtained sufficiently pure for analysis, being always contaminated with margaric acid, and an oily substance which is reddened by potash. It may be purified to a certain extent by dissolving it in ether, cooling the solution to  $0^{\circ}$  C., and washing the deposit with ether. *Elaidin* thus prepared bears considerable resemblance to stearin, and according to Meyer's analysis (Ann. Ch. Pharm. xxxv. 178), which gave 77.3 per cent. carbon and 12.0 hydrogen, may be regarded as tri-*elaïdin*,  $C^{54}H^{104}O^6 = C^{18}H^{32}O^2$  (glycerin) +  $3C^{18}H^{32}O^2$  (*elaïdic acid*) -  $3H^2O$  (calc.

7.73 carbon, and 11.7 hydrogen). It melts at 32° C., is nearly insoluble in alcohol, but dissolves readily in ether. By dry distillation it yields aerolein, elaidic acid, and hydrocarbons.

Elaidin is saponified by alkalis, yielding glycerin and a salt of elaidic acid. The *Unguentum oxygenatum* and *U. citrinum* of the pharmacopeias, prepared from hog's lard with nitric acid, contain impure elaidin.

**ELAIN.** Syn. with OLEIN.

**ELAIN-PHOSPHORIC ACID.** Syn. with OLEOPHOSPHORIC ACID.

**ELAIN-SULPHURIC ACID.** Syn. with OLEOSULPHURIC or SULPHOLEIC ACID.

**ELAIDIC ACID.** Syn. with RICINOLEIC ACID.

**ELAIONETER.** Berjot's name for a percolating apparatus, in which he exhausts oily seeds with sulphide of carbon, in order to determine the quantity of oil contained in them, by evaporating the sulphide of carbon and weighing the oil which remains. (Rép. Chim. app. ii. 160.)

**ELALDEHYDE.** A solid isomeric modification of aldehyde (i. 109). Lieben (Ann. Ch. Pharm. Suppl. Bd. i. 114) has shown that a similar modification may be obtained by treating aldehyde with iodide of ethyl.

**ELAONE.** Syn. with OLEONE.

**ELASMOSE.** Syn. with FOLIATED TELLURIUM. (See TELLURIUM.)

**ELASTIC BITUMEN.** Syn. with ELATERITE.

**ELASTIC TISSUE.** (Lehmann, *Physiological Chemistry*, iii. 49; also *Gmelin's Handbuch*, viii. 459. Handw. d. Chem. 2<sup>te</sup> Aufl. ii. [3] 667.)—The elementary fibres of this tissue are somewhat extensively distributed in the animal organism, though they never occur independently of other histological elements. They are most commonly found intermixed with the fibres of the connective tissue, very frequently also with smooth muscular fibres. They occur in the yellow elastic ligaments, as in the *Ligamenta flava* of the vertebral column, the inferior vocal chords, the *Ligamentum nucha* or neck-band of mammals, the elastic ligaments of the claws of the felidæ, and the hinge-ligament of bivalves. Large groups of elastic fibres connected into membranous sheaths are met with in the *fascia lata* and in the middle coats of the arteries and veins. Smaller accumulations of these fibres occur in many other parts, as, for instance, in the corium, and under the mucous membrane, more especially in the pharynx, the pylorus, cæcum, &c. The diameter of the elastic fibres varies considerably in different parts; thus, in the serous membranes, they are so fine as not to admit of exact measurement, whereas in the neck-band of some animals, they have a diameter of 0.004", and in the coatings of the arteries they are still broader.

The chemical basis of the elastic tissue, the so-called elastin, as obtained by boiling the tissue with alcohol, ether, water, strong acetic acid and dilute potash-ley, then with water, moderately strong hydrochloric acid, and again with water,—is a brittle, yellowish, distinctly fibrous mass, which when immersed in water, dilute ammonia or acetic acid, swells up and recovers its elasticity completely. It is quite insoluble in water, even after several days' boiling, thereby differing essentially from the true connective tissue, which is converted into gelatin by boiling with water. Elastin is likewise insoluble in alcohol, ether, and acetic acid. Strong potash-ley dissolves it with brownish colour: the solution, neutralised with sulphuric acid, does not gelatinise on evaporation, and is not precipitated by any acid excepting tannic acid. Elastin prepared as above burns without residue on platinum foil, and is free from sulphur. When boiled for some time with sulphuric acid, it yields leucine.

Purified elastic tissue from the neck-band of the horse has been analysed by Tilanus and W. Müller, with the following results:

	Tilanus.		W. Müller.			
Carbon . . .	54.90	55.65	55.47	55.72	55.65	55.09
Hydrogen . . .	7.25	7.41	7.54	7.67	7.11	7.33
Nitrogen . . .	17.62	17.74	16.09	15.71	16.62	16.43
Oxygen . . .	20.33	19.20	20.90	20.90	20.82	21.15
	100.00	100.00	100.00	100.00	100.00	100.00

**ELASTICITY** is the power possessed by many bodies of recovering their original shape and size, as soon as the external forces which altered them have ceased to act. There is perhaps no substance in which this power is altogether absent, but in some



bodies, moist clay for example, it exists in so slight a degree that, for all practical purposes, they may be regarded as inelastic. The elasticity of a body is perfect or imperfect, according as it recovers its original shape and size wholly or partially on the removal of the disturbing force.

*Elasticity of Gases.*—Gases not only yield to pressure and expand to their original bulk on the removal of that pressure, but their particles exhibit a constant tendency to fly asunder, so that a gas exerts a constant pressure against the sides of the vessel in which it is enclosed.

The elastic force of a gas is measured by the pressure which it is capable of sustaining, or by the pressure required to keep it within a given volume. Observation shows that the elastic force of the air at the earth's surface is capable of sustaining a column of mercury of the average height of thirty inches, which is equivalent to a weight of about fourteen pounds on the square inch; more exactly, when the height of the barometric column reduced to 0° C. is 760 millimetres, the pressure on a square metre is  $0.760 \times 1000 \times 13.596 = 10333$  kilogrammes, or 1.0333 kilogrammes on a square centimetre.

To measure the elastic force of a quantity of air in an enclosed space, the open end of a barometer-tube is connected with this space, as in the barometer-gauge of the air-pump. If the gas is confined by a liquid, as in a jar standing over water or mercury, the difference of level of the liquid without and within the tube must be taken into account. This difference of level must be reduced to its equivalent in mercury

by multiplying by  $\frac{d}{13.596}$  ( $d$  being the specific gravity of the liquid, and 13.596 that

of mercury), and the product added to or subtracted from the height of the barometer, according as the level of the liquid within the gas-jar is below or above that without.

If the gas stands over mercury, the preceding factor is reduced to 1; if over water, it is

$\frac{1}{13.596} = 0.073551$ .

The elastic force of a gas at a given temperature varies inversely as its volume. This law, called Boyle's or Mariotte's law, has been demonstrated experimentally up to pressures equal to twenty-seven times the ordinary pressure of the atmosphere, for gases capable of bearing that pressure without liquefaction. At pressures near those at which liquefaction takes place, the elasticity does not vary in the exact inverse ratio of the volume.

*Elasticity of Liquids.*—Liquids when subjected to pressure undergo a certain diminution of volume, and return to their original volume when the pressure is removed. The contraction produced even by very great pressures, is, however, very small, and consequently liquids were for a long time supposed to be absolutely incompressible; this conclusion was, moreover, supposed to be directly established by certain experiments made by the Florentine Academicians in the seventeenth century, in which closed metallic vessels completely filled with liquids were subjected to strong pressure or hammering; the vessels became cracked and the liquid oozed out, and this was regarded as a proof of its incompressibility. Canton in 1761 first attacked the problem in the right way, by subjecting liquids in thermometer-shaped vessels to strong pressure under the receiver of a condensing pump. These experiments established the fact of the compressibility of liquids, and subsequent researches by Perkins (Gilb. Ann. lxxii. 173; Pogg. Ann. ix. 547), by Oersted (Ann. Ch. Phys. [2] xxii. 190), and by Colladon and Sturm (Pogg. Ann. xii. 39), made with somewhat similar apparatus, afforded further proof of the compression, and determined its amount for several liquids. Subsequently experiments were made by Aimé (Ann. Ch. Phys. [3] viii. 257) on the coast of Algeria, by sinking thermometer-shaped vessels, attached to cords, in the sea, by which they were subjected to a pressure of 200 atmospheres.

Regnault has also made experiments on the compressibility of liquids by means of an instrument called a *piezometer*, consisting of a vessel like a thermometer with a cylindrical bulb and a graduated stem to hold the liquid; this vessel was enclosed in a strong vessel filled with water, and having a piston working water-tight in its neck, to communicate the pressure, and the whole was enclosed in a larger vessel of water to keep the temperature constant. In these experiments, the compression of the glass-vessel was directly determined, whereas former observers had determined this point from other observations, and not always with the same kind of glass. Lastly, Grassi (Ann. Ch. Phys. [3] xxxi. 437) has continued these experiments with the same apparatus, but using a more exact method of determining the compression of the glass vessel.

The following table gives the compressibility of several liquids, as determined by Grassi; the number for mercury is calculated from Regnault's experiments. The column headed "compressibility" shows the diminution in volume of a unit-volume

of the liquid when the pressure upon it is increased by 1 atmosphere. The column headed "pressure in atmospheres" shows the pressure to which the liquid was actually subjected; where blanks are left in this column, the superadded pressure was equal to 1 atmosphere.

*Compressibility of Liquids (Grass).*

Liquid.	Temperature.	Compressibility.	Pressure in atmospheres.
Mercury	0.0°	0.00000295	
Water	0.0	0.0000503	
"	1.5	0.0000515	
"	4.1	0.0000499	
"	10.8	0.0000480	
"	13.4	0.0000477	
"	18.0	0.0000463	
"	"	0.0000460	
"	25.0	0.0000456	
"	34.5	0.0000453	
"	43.0	0.0000442	
"	53.0	0.0000441	
Ether	0.0	0.000111	3.408
"	0.0	0.000131	7.820
"	14.0	0.000140	1.580
"	13.8	0.000153	8.362
Alcohol (absolute)	7.3	0.0000828	2.302
"	7.3	0.0000853	9.450
"	13.1	0.0000904	1.570
"	13.1	0.0000991	8.970
Wood-spirit	13.5	0.0000913	7.000
Chloroform	8.5	0.0000625	1.267
"	12.0	0.0000648	1.309
"	12.5	0.0000763	9.200
CaCl <sub>2</sub> -solution: 23.049 p. c. salt	17.5	0.0000306	
" " 40.99 " "	15.8	0.0000206	
" " 40.99 " "	41.25	0.0000229	
NaCl-solution: 24.004 p. c. salt	18.1	0.0000257	
" " 24.004 " "	39.6	0.0000263	
" " 15.323 " "	18.5	0.0000321	
KI-solution: 58.67 p. c. salt	15.5	0.0000260	
NaNO <sub>3</sub> -solution: 27.254 p. c. salt	18.1	0.0000295	
Na <sub>2</sub> CO <sub>3</sub> -solution: 17.185 p. c. salt	16.6	0.0000297	
Sea-water	17.5	0.0000437	
H <sup>+</sup> SO <sup>4</sup> + H <sup>2</sup> O	13.6	0.0000242	
H <sup>+</sup> SO <sup>4</sup> + 2H <sup>2</sup> O	14.6	0.0000250	
H <sup>+</sup> SO <sup>4</sup> + 3H <sup>2</sup> O	16.5	0.0000271	
H <sup>+</sup> SO <sup>4</sup> + 4H <sup>2</sup> O	14.7	0.0000279	
H <sup>+</sup> SO <sup>4</sup> + 5H <sup>2</sup> O	14.2	0.0000283	
H <sup>+</sup> SO <sup>4</sup> + 9H <sup>2</sup> O	14.6	0.0000315	

The compressibility of mercury, according to the older mode of calculation, is 0.000003517; the compressibility of de-aerated water at a given temperature is proportional to the pressure; the same is true for saline solutions and dilute sulphuric acid. In ether, alcohol, wood-spirit, and chloroform, the amount of compression increases more rapidly than the pressure. In different solutions of the same salt, the compressibility is smaller as the quantity of salt dissolved is greater. The compressibility of water decreases with rise of temperature; that of ether and of alcohol increases with the temperature. Water appears to exhibit a maximum of compressibility between 0° and 4.1 C.

The following table contains the results obtained by Colladon and Sturm and by Aimé; they agree very nearly with the preceding, excepting in the case of mercury. According to Colladon and Sturm, however, the compressibility of alcohol and ether decreases as the temperature rises.



*Compressibility of Liquids (Colladon and Sturm; Aimé).*

Liquid.	Pressure.	Compressibility.	Observation.
	Atmosph.		
Mercury at 0° C. . . . .	1—24	0·00000503	C. and S.
" 12·6° C. . . . .	"	0·0000040	Aimé.
Water at 0° C., free from air . . . .	1—24	0·0000513	C. and S.
" " containing air . . . . .	2—6	0·0000505	"
Water, sweet, at 12·6° C. . . . .	"	0·0000502	Aimé.
Sea-water at 12·6° C. . . . .	"	0·0000413	"
Water saturated with ammonia at 10° C. .	1—4	0·0000380	C. and S.
" " " " " " " " " " " " " " " "	4—16	0·0000350	"
Acetic acid at 0° C. . . . .	4—16	0·0000422	"
Acetic acid of 0·6° B. at 12·6° C. . . .	"	0·0000512	Aimé.
Nitric acid, spec. grav. 1·403, at 0° C. .	1—32	0·0000322	C. and S.
Sulphuric acid, concentrated, at 0° C. .	1—16	0·0000320	"
" " " " " " " " " " " " " " " "	"	0·0000332	Aimé.
Oxalic acid, saturated, at 11° C. . . .	"	0·0000479	"
Hydrochloric acid of 23° B. at 12·6° C. .	"	0·0000432	"
Ammonia at 12·6° C. . . . .	"	0·0000376	"
Sulphate of sodium, 13·8° B. . . . .	"	0·0000444	"
Alcohol (spec. grav. ?) at 11·6° C. . . .	1—8	0·0000962	C. and S.
" " " " " " " " " " " " " " " "	8—16	0·0000935	"
" " " " " " " " " " " " " " " "	16—24	0·0000890	"
Alcohol of 32° B. at 12·6° C. . . . .	"	0·0000682	Aimé.
Alcohol of 40° B. at 12·6° C. . . . .	"	0·0000996	"
Ether at 0° C. . . . .	1—12	0·0001330	C. and S.
" 0° C. . . . .	12—24	0·0001220	"
" 11·4° C. . . . .	1—12	0·0001500	"
" 11·4° C. . . . .	12—24	0·0001410	"
Nitrous ether at 0° C. . . . .	1—24	0·0000715	"
Chloride of ethyl at 11·2° C. . . . .	1—12	0·0000859	"
" " " " " " " " " " " " " " " "	6—12	0·0000823	"
Acetic ether at 0° C. . . . .	1—8	0·0000793	"
" " " " " " " " " " " " " " " "	8—16	0·0000713	"
Oil of turpentine at 0° C. . . . .	1—4	0·0000884	"
" " " " " " " " " " " " " " " "	4—16	0·0000730	"
" " " " " " " " " " " " " " " "	"	0·0000657	Aimé.
Naphtha at 12·6° C. . . . .	"	0·0000756	"

*Elasticity of Solids.*—The phenomena of elasticity in solid bodies are much more complicated than in liquids or in gases. Solids can be extended as well as compressed, or they may be compressed in one direction and at the same time stretched in another, as when a rod or plate is bent; and lastly they may be twisted, which effect may take place with or without compression or extension. When the alteration in size or form of a solid body is not carried beyond a certain limit, different for each body, the particles return exactly into their former relative positions on the removal of the disturbing force; in other words, within this limit of elasticity, the body is perfectly elastic. Beyond this limit, the alteration of form or size is more or less permanent, the molecules of the body no longer returning exactly to their former relative positions, as in malleable and ductile bodies, which retain whatever form is given them by strong pressure or hammering.

For some kinds of iron, the limit of elasticity corresponds to a tension of about 14 kilogrammes for each square millimetre of the transverse section; for other kinds, about 20 kilogrammes. If a bar or wire of iron be stretched by a force less than this, the extension is found to be proportional to the stretching force applied; beyond this limit, the extension increases more rapidly than in the direct ratio of the force, the wire becoming permanently stretched; and when the tension is increased to about 40 kilogrammes per square millimetre, the wire breaks. Other metals exhibit similar relations.

The coefficient of elasticity is the extension produced on the unit of length, by the unit of tension exerted upon the unit of transverse section; the reciprocal of this number is called the modulus of elasticity. Suppose a prismatic rod whose



length is  $l$  and transverse section  $c$ , to receive the elongation  $l'$  by a force  $P$ , within the limit of elasticity, pulling in the direction of its length; then  $\frac{P}{c}$  is the tension exerted on the transverse section 1, and  $\frac{l'}{l}$  the elongation produced by this force in the length 1. Consequently  $\frac{l'}{l} : \frac{P}{c} = \frac{lc}{lP}$  is the coefficient of elasticity, and  $\frac{lP}{lc}$  the modulus of elasticity of the rod. If the modulus be denoted by  $E$ , the elongation  $a$  produced by the stretching force  $S$  on the transverse section 1 will be  $a = \frac{S}{E}$ , or if  $\epsilon$  be the coefficient of elasticity,  $a = Se$ . The length of the rod being  $l$ , the elongation of the rod by the tension  $S$  (or  $\frac{P}{c}$ ) is  $la$ ; consequently  $l' = la = \epsilon \frac{Pl}{c} = \frac{Pl}{cE}$ .

Similar formulæ apply to the case of compression;  $E$  and  $F$  have then the same values as for tension, but the modulus of elasticity will perhaps have a different value. The equation  $Ea = S$  shows that the modulus of elasticity is the tension which would produce the unit of elongation, that is to say, would stretch the rod to twice its primitive length, supposing that it would conform to the laws of elasticity up to that limit, instead of breaking, as most bodies would do, long before. The only substance that will bear such an amount of tension without disruption is vulcanised caoutchouc.

The following table gives the moduli of elasticity, expressed in kilogrammes, for a transverse section of 1 square millimetre, of certain metals and alloys. The numbers in the last two columns were not obtained with the same wires as those in the first three.

Name of metal.	Specific gravity.	Modulus of Elasticity.				
		Of the annealed metal.			Of the unannealed metal.	
		at 15°-20° C	at 100° C.	at 200° C.	at 10° C.	at -15° C.
Lead . . . . .	11.232	1727	1630	.. .	.. .	.. .
Gold (pure) . . . . .	18.035	5585	5408	5482	8603	9351
Silver (pure) . . . . .	10.304	7145	7274	6374	7411	7800
Palladium . . . . .	11.225	9789	.. .	.. .	10289	10659
Copper . . . . .	8.936	10519	9827	7862	12200	13052
Platinum . . . . .	21.083	15518	14178	12964	15647	16224
Iron . . . . .	7.757	20794	21877	17700	.. .	.. .
Iron-wire . . . . .	7.553	.. .	19986	.. .	18613	17743
Cast-steel . . . . .	7.719	19561	19014	17926	.. .	.. .
Steel-wire (English) . . . . .	7.622	17278	21292	19278	.. .	.. .
Steel wire (tempered blue) . . . . .	7.420	.. .	18977	.. .	18045	17690
Brass . . . . .	8.247	.. .	.. .	.. .	9005	9782

The modulus of elasticity of an alloy is nearly the mean between those of the component metals. The passage of an electric current somewhat diminishes the modulus of elasticity of a metal (independently of the diminution consequent on the rise of temperature, produced at the same time), the effect ceasing, however, with the passage of the current. (Wertheim.)

Crystallised bodies not belonging to the regular system exhibit different degrees of elasticity in different directions.

**ELATERIN.** A substance contained in the fruit of the spirting cucumber (*Momordica Elaterium*), whence it may be extracted by boiling alcohol, and purified by precipitation with water, washing with ether, and recrystallisation from hot alcohol. It forms colourless hexagonal tables, fusible, decomposable by heat, insoluble in water, sparingly soluble in ether, very soluble in alcohol. It dissolves in sulphuric acid, forming a red liquid, which, when diluted with water, deposits a brown substance. Nitric acid dissolves elaterin without alteration. Elaterin is precipitated from its alcoholic solution by acetate of lead and nitrate of silver. Taken internally, it acts as an emetic and as a purgative. It gives by analysis 69.23 to 69.49 p. c. carbon, and

8.23 to 8.21 hydrogen, agreeing nearly with the empirical formula  $C^{20}H^{14}O^4$ . (Zwenger, Ann. Ch. Pharm. xliii. 369.)

**ELATERITE.** *Elastic bitumen. Mineral caoutchouc.* A fossil resin resembling asphalt, occurring in soft, flexible, somewhat elastic masses, at Castleton in Derbyshire, in a coal mine at Montrelais near Nantes at the depth of 230 feet, also at Neufchatel, and on the island of Zante. Specific gravity of the Derbyshire variety = 0.9053 to 1.233. Lustre, resinous. Colour, blackish-brown of various shades. Subtranslucent, sometimes exhibiting a dark orange-red colour by transmitted light. It takes fire readily, and burns with a lively yellow flame, emitting a bituminous odour. According to Johnston (Phil. Mag. 1838, July 23), it is a hydrocarbon containing 83.7—85.5 carbon, and 12.5—13.28 hydrogen. Henry (Ann. Phil. 1826, p. 70), on the other hand, found from 36.75 to 40.10 oxygen, whence Rammelsberg (*Mineralchemie*, p. 966) concludes that it consists mainly of a hydrocarbon  $C^8H^{12}$ , but mixed with an oxygenated compound.

**ELATERIUM.** The extract obtained by evaporating the juice of the fresh fruit of the spitting cucumber (*Momordica Elaterium*). It has a greenish or green-brown colour, a sharp bitter taste, and acts as a drastic purgative and an emetic. It contains elaterin, together with starch, resin, &c.

**ELATHIN.** An oily body produced by the action of ammonia and sulphur on acetone, and passing over on distillation between 120° and 200° C. (Zeise, Ann. Ch. Pharm. xlvii. 43.)

**ELATIN.** Syn. with ELATERIN.

**ELAYL.** Syn. with ETHYLENE.

**ELECAMPIN.** Syn. with INULIN.

**ELECTRICITY.** (Robison's *Mechanical Philosophy*, edited by Brewster, London, 1822, iv. 1. — Roget, *Library of Useful Knowledge: Natural Philosophy*, vol. ii. London, 1828. — Becquerel, *Traité expérimental de l'Électricité et du Magnétisme*, 7 tomes, Paris, 1834–1840. — Faraday, *Experimental Researches in Electricity*, 3 vol., London, 1839–1855. — J. Müller, *Lehrbuch der Physik und Meteorologie*, 2 Bände. Braunschweig, 1853. Bd. ii. S. 61. — P. T. Riess, *Die Lehre der Reibungs-electricität*, 2 Bände. Berlin, 1853. — De la Rive, *Traité d'Électricité théorique et appliquée*, 3 tomes, Paris, 1854–1858.

The phenomena displayed by rubbing a piece of amber, constitute one of the earliest physical facts recorded in the history of science. Thales, of Miletus, ascribed its mysterious power of attracting and repelling light bodies to an inherent soul or essence, which, awakened by friction, went forth and brought back the small particles floating around. In times near to our own, the same hypothesis was resorted to by Robert Boyle. From *ἤλεκτρον*, the Greek name of amber, the name "electricity" has been applied to the science which investigates the attractions and repulsions, the emission of light, explosions, and a variety of physical and chemical phenomena, which are produced, not only by the friction of vitreous, resinous, and metallic surfaces, but by various other modes of mechanical disturbance, by heat, by chemical action, and by magnetism.

If we rub a glass tube with a dry hand or a silk handkerchief, and then approach it to bits of paper or cotton, feathers, gold leaf, it will first attract these bodies, and then repel them. If the tube be held parallel to a table on which they have been laid, an electrical dance will be performed.

In a dark room, flashes of bluish light will be seen to play about the surface of the tube, while it is being rubbed, and on approaching the knuckle to it, a spark will pass between the two, accompanied by a snapping noise.

If to the farther end of the tube we hang a brass ball, by a thread of linen, hemp, or a metallic wire, the ball will participate with the rubbed tube in its attractive powers. But if the ball be suspended by a cord of silk, worsted, or hair, or by a rod of glass, wax, or pitch, the attractive and repulsive virtue will not pass into it.

This last experiment shows that the electric power, when developed, passes easily through some bodies and not through others. The former are called conductors of electricity; the latter non-conductors, or insulators. These last terms must not, however, be taken in their absolute sense; there is no known body which is absolutely destitute of the power of conducting electricity: in fact, there is a regular gradation of power from the best conductors to the worst.

1. The following is a list of conductors of electricity—that is to say, of bodies through which that power passes without much resistance—arranged in the order of their conducting power, the best conductors standing at the head of the list.

The metals  
Charcoal  
Plumbago  
Strong acids  
Soot and lamp-black  
Metallic ores  
Metallic oxides  
Dilute acids  
Saline solutions  
Animal fluids  
Sea-water

Rain-water  
Ice and snow above 0° F.  
Living vegetables  
Living animals  
Flame  
Smoke  
Vapour  
Salts  
Rarefied air  
Dry earths  
Massive minerals.

The metals differ greatly among themselves in conducting power: the methods of estimating their relative conducting powers will be described hereafter.

2. The following is a list of electrical non-conductors, in the inverse order of their insulating power:—

Dry metallic oxides, including fused alkaline and earthy hydrates  
Oils, of which the densest are best  
Ice below 0° of Fahr.  
Phosphorus  
Dry chalk and lime  
Lycopodium  
Caoutchouc  
Camphor  
Massive minerals, non-metallic  
Marble  
Porcelain  
Baked wood, and dried vegetables  
Dry paper, parchment, and leather

Dry gases  
Wool, hair, and feathers  
Dyed silk  
Bleached silk  
Raw silk  
Glass, and all vitrified bodies, comprehending diamond and crystallised transparent minerals  
Asphaltum  
Wax  
Sulphur  
Resins, including gutta percha  
Amber  
Shellac.

Gutta percha possesses very great insulating power, but its place in the list has not been determined with certainty; indeed its insulating power varies considerably with its quality. Gun-cotton and collodion are likewise excellent insulators.

All bodies are capable of becoming electric by friction; but to enable a conducting body to exhibit this power when excited, it must be *insulated*, that is to say, cut off from electric communication with the ground: thus, if we hold a brass rod in the hand and rub it, no signs of electricity will be apparent, because the electricity, as fast as it is developed, passes along the rod into the hand which holds it, thence through the body, which is made of conducting materials, into the ground, where it is lost by diffusion; but if a metal cylinder be supported on a stem of glass, gutta-percha, or shellac, or suspended by silk cords, and then rubbed with flannel or beaten with a cat-skin, it will acquire the property of attracting light bodies.

It was formerly supposed that conducting bodies could not be excited by friction: hence they were called non-electrics, non-conducting bodies being called electrics; the latter term is still often applied to bodies, like glass and shellac, which are the most easily excited by friction.

When an excited electric is brought in contact with another non-conducting body, the part of the latter touched by the excited body becomes electrical, but the power does not spread over its surface; but when one point of an insulated metal rod or ball is touched by an excited electric, the power is immediately communicated to every part of it; and if the conductor thus electrified be touched by another insulated conductor, the whole surface of that conductor immediately becomes electrified, acquiring the power of giving sparks and attracting light bodies, and at the same time the electric power of the first conductor is diminished in intensity. In fact, the electric power originally possessed by the one is now distributed between the conductors in the proportion of their surfaces.

The facility with which electricity is communicated from one conducting body to another, renders the complete insulation of conductors of great importance in all electrical experiments. Light bodies, such as balls of elder-pith, feathers, &c., used to exhibit attraction and repulsion, are suspended by silk cords: metallic conductors are supported on rods of glass, gutta-percha, shell-lac, or sealing-wax. The air when dry is an insulator: indeed, if this were not the case, it would be scarcely possible to obtain any manifestation of electric power, as it would be dissipated into the atmosphere as fast as it was developed; and, in fact, in a damp atmosphere it is very difficult to retain the electric power on the surface of any excited body, as the aqueous vapour



possesses considerable conducting power. Moreover, the atmospheric moisture quickly condenses on the insulating supports, especially on glass and silk, and completely destroys their insulating power; hence it is of great importance, when working in a damp atmosphere, to keep the insulating supports as warm as possible, and to rub them frequently with a dry cloth. The insulating power of glass is greatly increased by covering it with copal varnish.

The insulating power of air is likewise diminished by heat; indeed very hot air conducts with great facility. The best way of depriving an excited non-conductor of its electric charge is to move it about for a while a few inches above the flame of a spirit-lamp.

#### OF THE TWO ELECTRICITIES.

The phenomena above mentioned, that is to say, the attraction and subsequent repulsion of light bodies, and the production of the electric light, are manifested by all bodies whatever, when in a state of electric excitement, whether brought into that state by friction, or by communication with a previously excited body. In certain respects, however, the electric powers excited in different bodies are opposed to, and capable of neutralising, one another.

Rub a glass tube with silk, and bring it near a feather suspended by a silken cord; the feather will approach the glass, remain in contact with it for a short time, then fly off, and will afterwards be persistently repelled by the glass. Now rub a piece of sealing-wax with flannel, and bring it near another feather suspended on silk: the same phenomena will take place; but, on the other hand, the feather which is repelled by the excited glass is attracted by the excited wax, and that which is repelled by the wax is attracted by the glass. Moreover, the two feathers thus electrified attract each other, whereas two feathers electrified by contact, either with the glass or with the wax, repel each other.

There are, then, two kinds of electric force, exactly similar in certain of their manifestations, but directly opposed in others. One of these powers, which is developed most frequently, though not invariably, on glass, is sometimes called *vitreous electricity*; and the other, which is most frequently manifested by resinous and waxy bodies, is called, *resinous electricity*. The phenomena above described may be summed up as follows:—*Bodies similarly electrified* (both vitreously or both resinously) *repel each other, and bodies dissimilarly electrified* (one vitreously and the other resinously) *attract each other*.

Neither of these electric powers is ever manifested without the other, though from the manner in which the excitement is produced, it frequently happens that only one becomes apparent. Experiment shows, that in all cases whatever, when two bodies are rubbed together, one becomes vitreously, the other resinously electrified. Thus, if a stick of sealing-wax be rubbed with a piece of flannel attached to the end of a glass rod or a stick of baked wood, the wax will acquire resinous, the flannel vitreous electricity, the one attracting a feather or pith-ball which has been in contact with and is repelled by the other. In like manner it may be shown, that when glass is rubbed with silk, the glass becomes vitreously, the silk resinously electrified. If the rubber in either case, instead of being fixed on an insulating support, be held in the hand, the electricity which it acquires cannot show itself, because it passes through the body into the ground.

The kind of electricity which any given substance acquires by friction is not always the same, but varies according to the nature of the substance against which it is rubbed. Thus, woollen cloth becomes vitreously electrified when rubbed against wax or resin, resinously when rubbed against glass; glass itself becomes resinous when rubbed with a cat-skin, vitreous when rubbed with cloth. The following table, taken from De la Rive, gives a list of substances, each of which becomes vitreously electrified when rubbed with either of those which follow it; resinously, when rubbed with either of those which precede it:—

The skin of a cat  
Diamond  
Flannel  
Ivory  
Rock-crystal  
Wool  
Glass  
Cotton  
Linen cloth  
White silk  
The dry hand

Wood  
Sealing wax  
Colophony  
Amber  
Sulphur  
Caoutchouc  
Gutta percha  
Prepared paper  
Collodion  
Gun-cotton.

No visible relation can be pointed out between the nature or constitution of the substances, and the species of electricity which is developed by their mutual friction. The only general law among the phenomena is, that the rubbing and the rubbed body always acquire opposite electricities. Sulphur is vitreously electrified when rubbed with every metal except lead, and resinously with lead and every other kind of rubber. Resinous bodies rubbed against each other acquire alternately the vitreous and resinous electricity; but, rubbed against all other bodies, they become resinously electrical. White silk acquires vitreous electricity with black silk, metals, and black cloth; and resinous with paper, the human hand, hair, and weasel's skin. Black silk becomes vitreously electrical with sealing-wax, but resinously with hares', weasels', and ferrets' skins; also with brass, silver, iron, the human hand, and white silk. Woollen cloth is strongly vitreous with zinc and bismuth; moderately so with silver, copper, lead, and specular iron. It is resinous with platinum, gold, tin, antimony, grey copper, proto-sulphide and hemisulphide of copper, and the sulphides of silver, antimony, and iron. When two ribands of equal surface are excited by drawing one lengthwise over a part of the other, that which has suffered friction in its whole length becomes vitreously, and the other resinously, electrical. Silk stuffs agitated in the atmosphere with a rapid motion, always take the resinous electricity, while the air becomes vitreously electrified. The general result which was deduced by Coulomb, from his very numerous and exact experiments on this subject, is the following:—

When the surfaces of two bodies are rubbed together, that whose component parts recede least from each other, or are least disturbed from their natural position of repose, appear, in consequence, more disposed to assume the vitreous electricity: this tendency augments if the surface experiences a transient compression. Reciprocally, that surface whose particles deviate most from their ordinary position, by the violence of the other, or by any cause whatever, is, for that reason, more disposed to take the resinous condition. This tendency increases if the surface undergoes a real dilatation. The stronger this opposition of circumstances, the more energetic is the development of electricity on the two surfaces. It grows feebler in proportion as their state becomes more similar. Perfect equality would nullify the phenomena, provided it could exist. Thus, when a dry animal or vegetable substance is rubbed against a rough metallic surface, it exhibits signs of resinous electricity: in this case, its parts are forcibly separated. When, on the other hand, it is rubbed on a polished metal, which scarcely affects its surface, or merely compresses the particles, it either affords no evidence of electricity, or it exhibits the vitreous kind. Heat, by dilating the pores, acts on the surfaces of bodies as a coarser rubber would do. It disposes them to take the resinous electricity. Thus, also, new black silk, strongly dyed, being rubbed against a riband of white, takes always the resinous electricity. But when the black stuff is worn, and the colour faded, if we open the pores of the white riband by heat, this acquires in its turn a greater tendency to the resinous electricity than the black silk, and consequently makes it vitreous. This disposition vanishes, as might be expected, with the accidental cause that produced it; and the white riband, on becoming cold, reacquires the vitreous electricity. The black dye produces on wool the same effect as on silk. A white riband, rubbed against white woollen stuff, always gives signs of resinous electricity; but, against wool dyed black, it affords signs of vitreous electricity.

There are several other ways, besides friction, of developing electricity, viz., by heat, by magnetism, by chemical action, and by the change of state of bodies from the solid to the liquid and gaseous, and *vice versa*; but it is better to defer their consideration till we have considered the principal properties and effects of electricity developed by friction.

*Theory of Electricity.*—The facility with which electricity is communicated from one body to another, and makes its way to all parts of a conducting body, or chain of conductors, however complex in form, gave rise, at an early stage of the science, to the idea that it is a fluid; and the discovery of the opposite characters of vitreously and resinously electrified bodies further led to the hypothesis that there exist two such fluids or at least two modifications of the same fluid, which, when they exist together, neutralise each other's effect, but when separated manifest themselves in the several ways already noticed.

Reserving for a future part of this article the discussion as to the comparative merits of this theory and others which have been proposed for explaining the phenomena of electricity, we shall for the present regard it merely as a convenient mode of linking together, and generalising those phenomena,—presenting it for this purpose in the form of the following propositions:

1. All bodies contain two very mobile, elastic, imponderable fluids, called the electric fluids.
2. The particles of each of these fluids repel each other, and attract those of the



other fluid, with forces which are equal at equal distances, but diminish with increase of distance.

3. These fluids are capable of passing from one body to another, and travelling over or through different bodies with different degrees of facility.

It is easy to see that the theory thus stated accords with all the phenomena hitherto described. When the two fluids are contained in a body in equal quantities, their attractive and repulsive forces, exerted on any particle of either fluid situated externally to that body, are equal, and neutralise each other, so that no electrical phenomena are apparent, but the body appears in its ordinary state. But when, by friction or otherwise, a separation of the fluids takes place, and one of them becomes accumulated on a body, or a particular part of a body, in greater quantity than the other, the excess will show itself by attractive and repulsive forces exerted upon the fluids contained in neighbouring bodies.

When two movable bodies, pith-balls for instance, are charged with the same kind of electricity (say vitreous), the excess of vitreous fluid in each is driven to the outer side, where its further progress is prevented by the air, through which it cannot readily pass; it there exerts a pressure on the two balls in opposite directions, causing them to recede from one another. If the two bodies are oppositely charged, the excess of vitreous electricity of the one, and the resinous electricity of the other, attract each other and accumulate on their contiguous surfaces, where they exert a pressure impelling the balls towards each other. If the balls actually come in contact, an interchange of the two electric fluids takes place between them, and if they were charged with equal quantities of the two fluids, their charges neutralise each other exactly, and both bodies return to their natural state, no longer appearing electrified. If the quantity of vitreous electricity on the one was larger than that of resinous electricity on the other, both appear vitreous after contact, and *vice versa*.

The neutralisation or union of the opposite electricities may also take place without actual contact. Suppose two brass balls supported on insulating stands to be oppositely electrified and gradually brought nearer to each other. As they approach, the opposite electric fluids will be drawn more and more to the nearest points of their surfaces, and at length the attraction between them will become strong enough to overcome the resistance of the intervening air. The union of the opposite electricities then takes place through the air in the form of an electric spark, longer and brighter, as the quantities of the opposite fluids present on the balls are greater. If the balls cannot be brought near enough, the union of their opposite electricities may be effected by connecting them by means of an insulated metal rod or other conductor. In either case, the balls after being connected, appear neutral or similarly charged, according as their opposite charges were equal or unequal.

The union of the opposite electricities in either of the ways above mentioned is called the electric discharge. In the case just considered, it is instantaneous; but suppose the two brass balls or other conducting bodies, to be connected, one with a constant source of vitreous, the other with a constant source of resinous electricity, and a communication made between them by a rod or wire of metal: in that case, an uninterrupted series of charges and discharges of the opposite electricities will take place along the conducting chain. This is called the electric current; we may suppose indeed that a stream of vitreous electricity is flowing through the conductors in one direction, and a stream of resinous electricity in the other, during the whole time that the action is kept up.

Electricity in the state of discharge, whether sudden or continuous, is called dynamic electricity, that is, electricity in motion; in the charged state it is called statical electricity, or electricity of tension.

The opposite electricities are now most frequently distinguished by the terms positive and negative, the former being used synonymously with vitreous, the latter with resinous electricity. It must be distinctly understood, however, that there is nothing in the first mentioned kind of electricity (that commonly developed on glass) to entitle it to be considered more positive than the other. The terms positive and negative as applied to the two electricities, are intended merely to indicate opposition of properties and the power of mutual neutralisation. It is often convenient to abbreviate them into  $+E$  and  $-E$ .

#### ELECTRICAL MACHINES.

For the study of electrical phenomena, it is necessary to have means of liberating the electric fluids in larger quantity than is possible by the simple apparatus hitherto mentioned. Machines for this purpose consist of a cylinder or circular plate of glass turning on a horizontal axis and rubbing against a cushion of silk or leather. The



glass thus acquires a charge of positive or vitreous electricity, which is transferred to an insulated metallic conductor.

Fig. 370 represents a cylinder machine. The cylinder rubs against the cushion, which is attached to a hollow brass cylinder supported on glass legs. To the upper edge of the cushion is attached a silk flap which lies over the upper part of the glass cylinder. On the other side of the glass cylinder is another brass conductor, called the *prime conductor*, also supported on glass legs, and having on the side next to the glass cylinder a row of pointed wires, fixed to it on a level with the axis of the cylinder; these are for the purpose of facilitating the passage of the electricity from the glass cylinder to the conductor, as will be presently explained.

The cushion is covered with an amalgam of mercury, tin, and zinc, mixed up to a pasty consistence with tallow-grease or lard. This amalgam is found to be the best of all excitors for glass. A good proportion of the ingredients is 65 pts. mercury, 24 tin, and 11 zinc. They should be melted together and constantly stirred. Bisulphide of tin is also a good material for covering the rubber; but it is troublesome to prepare.

On turning the cylinder, the glass acquires positive electricity, the cushion and the brass conductor attached to it negative electricity, and the positive charge of the glass is transferred to the prime conductor. If both conductors are insulated, the charge on each of them soon reaches its maximum; that is to say, the transfer of  $+E$  to the glass, and of  $-E$  to the cushion, soon becomes as great as the machine is capable of effecting; but if the negative conductor is connected with the ground by a brass chain or wire, the  $-E$  developed on the cushion is at once carried away, and an equal quantity of  $+E$  is transferred to the glass cylinder, and thence to the prime conductor, which will then give off its positive charge in long bright sparks to any conducting body brought near it. If, on the other hand, the positive conductor be connected with the ground, and the negative conductor insulated, the  $+E$  is continuously carried away into the earth, and an equal quantity of  $-E$  is transferred from the prime conductor to the glass cylinder, and thence to the negative conductor, which then acquires a high negative charge, and will also give bright sparks to any conductor presented to it. If both conductors are insulated, and jointed brass rods terminated by knobs inserted into them and brought within a short distance of each other, the  $+E$  and  $-E$  recombine in a continuous series of sparks as long as the machine is worked. If the terminal knobs are brought very close to each other, the sparks are small but more continuous than when the interval between the knobs is greater; and if the two knobs are brought into actual contact, no sparks pass, and, indeed, neither conductor shows any signs of charge, either by giving sparks or by attracting light bodies; nevertheless, as long as the machine is worked, the separation of the two electricities is going on at the surface of contact of the glass and cushion; the  $+E$  is being transferred to the one conductor, the  $-E$  to the other, and the two are continually reuniting along the connecting brass rods; in short, an electric current is established through the machine, and though it does not show itself in any of the ways just mentioned, may be made to produce a variety of effects which will be described hereafter.

The *plate-machine* represented in *fig. 371* will be understood without special description. Various forms are given to it. In that shown in the figure, which is the ordinary form, the rubber is uninsulated, so that there is no means of obtaining negative electricity, and to insulate the cushions of a plate machine introduces considerable complication. For this reason cylinder machines are the more convenient for the purpose of illustrating

Fig. 370.

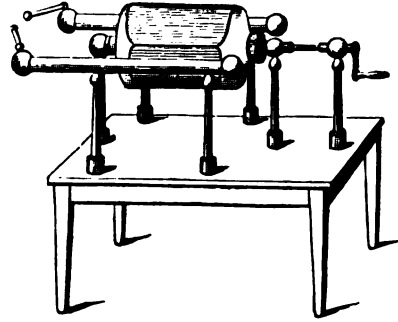
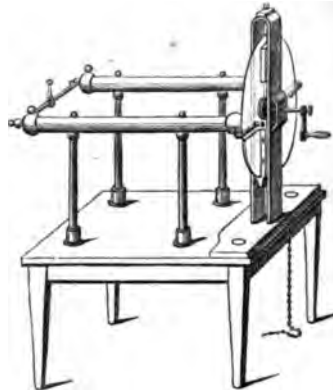


Fig. 371.



the principles of the science. When, on the other hand, it is merely required to obtain one kind of electricity, as for investigating the effects of the electric discharge or current on bodies through which it passes, plate machines are usually preferred, as they are more compact, and yield a greater quantity of electricity from a given surface of glass.

Recently, ebonite (hardened caoutchouc) has come much into use instead of glass for plate electrical machines; it produces powerful electric excitement, and does not condense moisture on its surface so readily as glass does; hence, while new, it is better adapted for use in damp weather; but the friction of the rubber destroys the polish of its surface, whereby its efficiency as a source of electricity is greatly diminished. The electricity obtained from the prime conductor of a machine with an ebonite plate is resinous or negative electricity.

#### ELECTROSCOPES AND ELECTROMETERS.

An *electroscope* is an instrument for indicating the presence of electricity in a state

Fig. 372.

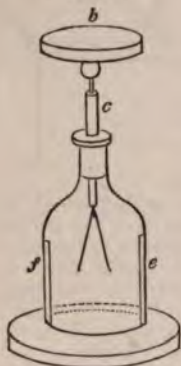
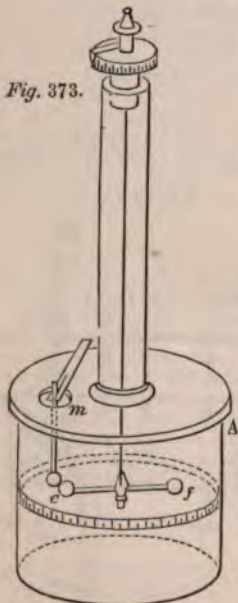


Fig. 373.



of charge or tension, by means of the attraction and repulsion of light bodies. In this sense any light body, such as a feather or a pith-ball, suspended by a silk line, may be regarded as an electroscope. Two pith-balls connected by a linen or cotton thread, which is a conductor, and hung over an insulated metal rod to which a charge is communicated, will indicate its presence by their divergence. For detecting small charges of electricity, the gold-leaf electroscope (fig. 372,) is a very convenient and indeed indispensable instrument. It consists of a glass jar open at both ends, and supported on a wooden stand covered with tin foil. The neck is closed with a cap, through which there passes a brass rod *c*, to the lower extremity of which are attached two strips of gold-leaf or Dutch metal; to the upper end of the rod *c* is attached a brass cap *b*. A charge of electricity communicated to this cap is immediately transferred to the leaves, and causes them to diverge. As a strong charge sometimes causes the leaves to strike against the sides of the glass, thereby giving it a charge of electricity, which, if retained, would disturb the indications of the instrument, two strips of tin foil, *ef*, are pasted on the inside of the jar, so that when the leaves strike against them, the charge may be immediately carried down into the stand, and thus got rid of. Where very great delicacy is not required, it is best to use leaves of Dutch metal, as they are easily replaced when injured; but for greater delicacy gold leaves must be used. The sensitiveness of the instrument is greatly increased by certain additions, to be afterwards described.

To test the kind and degree of charge of an electrified body by means of this instrument, the body is touched with a small brass ball suspended by a silk line, or with an instrument called a *proof plane*, consisting of a small disc of gilt paper attached to a thin stick of shellac, and the ball or plane is then brought in contact with the cap of the electroscope. The degree of divergence of the leaves gives an approximate indication of the strength of the charge; and its nature, whether positive or negative, may be known by holding above the cap an excited glass rod, which increases or diminishes the divergence of the leaves, according to the kind of electricity with which they are charged. For a description of Peltier's electroscope, see Peltier, (Ann. Ch. Phys. [2] lxii. 422), also Riess (*Reibungs-Electricität*, i. 64).

An *electrometer* is an instrument for measuring quantitatively the charge of an electrified body. The one most used is the torsion balance or torsion electrometer of Coulomb, represented in fig. 373. It consists of a glass case *A* (fig. 373),

of cylindrical or cubical form, surmounted by a vertical glass tube about 2 feet high; through the axis of the tube there passes a silver wire or a glass thread, carrying at its lower extremity a brass weight, which stretches it, and through which there passes a needle of shell-lac, terminated by gilt pith-balls, *e f*. The wire or glass thread is fastened at its upper extremity to a button, *b*, which moves stiffly in the cap, and carries an index, *i*, moving over a graduated circle, to measure the angle through which the thread is twisted. In the cover of the glass case there is a lateral aperture, *m*, for introducing a gilt pith ball attached to a shellac stem, this ball having the same diameter as those at the end of the needle (sometimes proof planes are substituted for the balls). This ball, after having been brought in contact with the body whose electric charge is to be measured, is introduced into the glass case, as shown in the figure, where it first attracts the ball *e*, and then having charged it, repels it to a certain distance, which may be measured in degrees on the divided circle. Now when a thread or wire is twisted, the force with which it tends to untwist increases in direct proportion to the angle of torsion. Thus, if one electric charge drives the movable ball to  $10^\circ$  from the fixed ball and another drives it  $20^\circ$ , the repulsive force in the second case is twice as great as in the first. But the usual mode of working with the torsion balance is, after having communicated the charge to the movable ball, and driven it off, to twist the thread the contrary way, till the movable ball is brought within a certain distance of the fixed ball. Suppose that this distance is  $10^\circ$ , and the thread has been twisted through  $20^\circ$ ; then the total force of torsion is  $30^\circ$ , for the thread is twisted through  $10^\circ$  at the bottom and  $20^\circ$  at the top. The use of the instrument will be illustrated by describing its application to the investigation of the

#### LAWS OF ELECTRIC ATTRACTION AND REPULSION.

1. *With regard to distance.*—Let the fixed ball be charged from the conductor of an electrical machine, and its charge communicated to the movable ball as above described. Suppose the movable ball to become stationary at  $36^\circ$  from the fixed ball, the thread or wire having been previously quite untwisted. Now let the wire be twisted till the movable ball is brought to  $18^\circ$  distance from the fixed ball; for this it will be found necessary to twist the wire through  $126^\circ$ , making the entire torsion equal to  $126^\circ + 18^\circ = 144^\circ$ . Next let the wire be further twisted till the distance between the two balls is reduced to  $9^\circ$ ; this will require the wire to be twisted through  $567^\circ$ , making the entire torsion  $= 567^\circ + 9^\circ = 576^\circ$ . The forces required to keep the balls at  $36^\circ$ ,  $18^\circ$ , and  $9^\circ$  apart are therefore as the numbers 36, 144, 576, that is to say, when the distances are as  $1 : \frac{1}{2} : \frac{1}{4}$ , the repulsive forces are as  $1 : 4 : 16$ ; hence the repulsive force exerted between two bodies similarly electrified varies inversely as the square of the distance.

In like manner by charging the fixed and movable balls with opposite electricities, it may be shown that the attractive force follows the same law.

2. *With regard to quantity.*—Coulomb's method of determining the manner in which the attractive or repulsive force between two electrified bodies varies with the quantities of free electricity contained in them, is based upon the obvious assumption that if two equal and similar insulated conductors, two equal metallic spheres, for example, be electrified and placed in contact, the electric charge will be divided equally between them. This being granted, the law in question may be investigated as follows:—Observe the force of torsion which at a certain distance equilibrates the attractive or repulsive force exerted between the fixed and movable ball of the torsion balance, which, as already observed, are of equal diameter. Now take a third gilt ball, likewise of the same size, and insulated, but not electrified, and touch with it the fixed ball of the balance. This contact deprives the fixed ball of half its electricity, the charge of the movable ball remaining unaltered. It will then be found that the force of torsion required to keep the balls at the same distance is only half what it was before. If the electricity of the movable ball be then reduced to one-half in the same manner, the force required to keep it at the same distance will be reduced to one-fourth of its original amount, and by again reducing the charge of either ball one-half, the force required will be reduced to one-eighth of the original amount. Hence: *At a given distance the attractive and repulsive forces exerted between two electrified bodies are as the product of the quantities of free electricity contained in them.*

If then *E, E'* are the quantities of free electricity in two bodies, and *D* the distance between them, the attractive or repulsive force between them is represented by the equation:

$$F = m \frac{EE'}{D^2}$$

*m* being a constant.



This law is, however, subject to modification, depending on the form of the body and on the mode of distribution of the electric charge upon it. Like the law of gravitation, it is strictly true only for material points, or for spheres, which act upon one another like material points situated at their respective centres, or for other bodies whose dimensions are insignificant as compared with the distances between them. Moreover, when two charged bodies are in presence of one another, the distribution of the charge on each is not the same as if the other were removed; and this also materially affects the magnitude of the resultant attractive or repulsive force exerted between them. Coulomb's experiments, which were made with spheres, may, however, be regarded as proving that the attraction and repulsion between the ultimate particles of the electric fluids follow the law of the inverse squares.

#### DISTRIBUTION OF ELECTRICITY.

In consequence of the mutual repulsion of the particles of each of the electric fluids, and the facility with which they can traverse conducting bodies, it follows, that any charge of electricity communicated to an insulated conductor will be confined to its surface, the interior remaining in the neutral state; for even if a charge of either electricity be communicated to the interior of a solid conductor, the mutual repulsion of its particles will drive it to the surface, where it will be retained by the insulating power of the air, or other surrounding non-conductor. The experimental proof of this proposition is easy. Charge an insulated metallic vessel of any shape whatever with electricity from the conductor of a machine; touch different parts of its surface with a proof-plane or carrier-ball, (p. 380), and then bring the plane or ball in contact with a gold-leaf electroscope; the external surface will be found strongly charged, while the inner surface exhibits no charge whatever, and this will be the case even though the external surface is charged sufficiently to give strong sparks.

It follows from this, that a charge of electricity is distributed between two conductors in contact in proportion to their surfaces, not to their masses. Coulomb gave experimental proof of this by observing the repulsive force between the two balls of the torsion balance, before and after the fixed ball had been touched with a third ball of exactly the same size, likewise insulated but unelectrified. Whether this third ball was solid or hollow, made of copper, lead, or any other metal, of wood, cork, or elder-pith, or, in short, of any conducting substance whatever, it always took away from the fixed ball of the torsion balance half the electricity which it possessed. If the unelectrified ball had a double surface, the electric charge of the fixed ball of the torsion balance was reduced to a third of its original amount; and in all cases, the charge was found to be distributed between the two in the proportion of their surfaces.

*Distribution of electricity on surfaces of different forms.*—When an insulated metallic sphere placed at a considerable distance from all other conducting bodies is charged with electricity of either kind, all the points of its surface are found to be charged in the same degree: this may be shown by means of the proof-plane and torsion balance, as already described. This uniformity of charge implies that the electric fluid is distributed over the surface of the sphere in a stratum of uniform thickness; for if there were more at one point than at another, the proof-plane would then receive a higher charge. This mode of distribution is a direct consequence of the law of variation of force according to the inverse squares of the distances. To show this, let the circle  $b g d$  (fig. 374) represent a section through the centre of a conducting sphere charged—say

Fig. 374.



with  $+E$ . It is clear that when the whole is in a state of equilibrium, any particle of positive electricity  $a$ , within the sphere must be equally repelled by the portions of electric fluid situated on opposite parts of the surface, and any particle of negative electricity equally attracted by such opposite portions. Draw through  $a$  two straight lines  $daf$ ,  $gah$ , making a small angle with each other, and suppose them to revolve round the line  $bac$  bisecting the angle  $dag$ . They will then trace out two small conical spaces, the bases of which are portions of the spherical surface. The condition of equilibrium of the particle  $a$  is that the action exerted upon it by the fluid on the portions of surfaces  $dg$  and  $fh$ , must be equal. Now the action of any particle in the surface  $dg$  on  $a$ , is to that of a particle in  $fh$  as  $(ac)^2$  to  $(ab)^2$ ; therefore, to ensure equilibrium, the quantity of electricity on the surface  $dg$  must be to that on  $fh$  as  $(ab)^2$  to  $(ac)^2$ ; but these

surfaces themselves are to one another in the same ratio; hence it follows, that the thickness of the stratum of electric fluid on  $dg$  must be the same as that on  $fh$ . If, for example,  $ab = 2ac$ , then the quantity of electricity on  $dg$  must be four times as great as that on  $fh$ ; but the surface  $dg = 4fh$ ; and it is evident that a fourfold quantity spread over a fourfold surface must form a stratum of the same thickness.

But in an oval-shaped body, such as that represented in section in *fig. 375*, a similar construction will show that the electric fluid must be accumulated in a thicker stratum towards the narrow ends. For in this case the surface  $dg$  bears to  $fh$  a ratio greater than that of  $(ab)^2$  to  $(ac)^2$ , greater therefore than the ratio of the quantity of electricity on  $dg$  to that on  $fh$ ; consequently, the thickness of the stratum of fluid in  $dg$  must be less than that on  $fh$ . In the case of an ellipsoid of revolution, mathematical analysis shows that the thicknesses of the electrical stratum at the ends of the axes are directly as the lengths of those axes; and this conclusion is confirmed by experiments with the torsion balance.

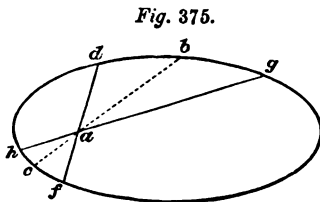


Fig. 375.

In general, all elongated conductors exhibit an excess of electrical charge towards their extremities. A cylinder 5 centimetres in diameter and 85 centimetres long, with hemispherical ends, was found by Coulomb to exhibit at the extremities an electric charge 2.3 times as great as in the middle; at 25 centimetres from the extremities, the charge was 1.25 times as great as in the middle. In a prismatic conductor, the distribution is similar; in a thin plate, the thickness of the electric stratum increases rapidly from the middle towards the edges. Now the tendency of electricity to escape from any part of a charged conductor, increases rapidly with the thickness of the stratum of electric fluid at that point, in consequence of the crowding together of a greater number of mutually repulsive particles within a given space. Hence it follows that elongated conductors, such as pointed rods, will discharge electricity much more rapidly than rounded ones; indeed, when a pointed rod or wire is inserted into the conductor of an electrical machine, it is impossible to obtain large sparks from it, however quickly the machine may be worked, the charge being rapidly dissipated from the point. Hence, to retain the charge on the surface of a conductor, that surface must be well polished, and free from all sharp projections.

The discharge of electricity from a pointed conductor gives rise to a rapid charging of the surrounding particles of air, and these particles becoming electrified, similarly to the conductor, are quickly repelled from it, and produce a wind, blowing as it were from the extremity of the conductor. Moreover, since the repulsion is mutual, if the pointed conductor be movable, it will be impelled in the opposite direction to the stream of air. Thus, if a cross formed of brass wires, having their ends bent in one direction, as in *fig. 376*, be supported by a cap on a pointed rod inserted into the conductor of an electrical machine in action, it will rotate in a direction opposite to that in which the points are turned.

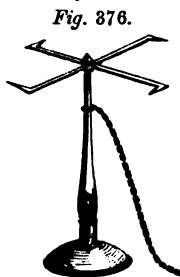


Fig. 376.

**Quantity and Intensity of Charge.**—The same quantity of electricity exhibits very different degrees of repulsive force, according to the way in which it is distributed. Thus a quantity of electricity which, when communicated to an insulated metallic ball, exerts a repulsive force equivalent to a torsion of  $10^\circ$ , will exert only half that force, or  $5^\circ$ , when distributed over two such spheres of the same diameter (p. 381). This is frequently expressed by saying that the *intensity* of the charge in the first case is double that in the second. Intensity, in fact, denotes the tendency of electricity to escape from any space in which it is confined, and its power of overcoming obstacles to its passage. The term is applied with reference to electricity much in the same way as *temperature* with respect to heat. Just as a pint of water at  $100^\circ$  C. can produce many effects which a gallon of water at  $50^\circ$  cannot, *e.g.* causing alcohol to boil, fat to melt, &c., although the quantity of heat in the latter (as measured by the quantity of ice that it will melt on cooling to  $0^\circ$ ) is greater than in the former; so likewise a small quantity of electricity confined in a small space exerts a much greater repulsive force than a larger quantity distributed over a comparatively larger space. The intensity of an electric charge is, in fact, proportional to the square of the thickness of the stratum of electric fluid on the surface of the charged body. For the repulsive force exerted between any two portions of the same electric fluid at a given distance varies

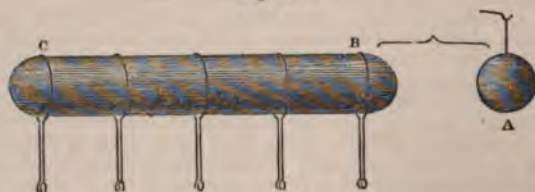


as the product of those quantities (p. 381), and if they are both increased  $n$  times, the repulsive force between them increases  $n^2$  times. Now the tendency of electricity to escape from a charged body arises from the repulsion exerted on the electricity at any one point of its surface by the total quantity of electricity of the same kind diffused over the rest of the surface. If now the quantity of free electricity contained in the body be doubled, the thickness of the superficial stratum will be doubled at all points; consequently the repulsive force between the portions of electricity at any two points will be quadrupled. And, in general, if the quantity is increased  $n$  times, the intensity or tendency to escape increases  $n^2$  times.

#### DEVELOPMENT OF ELECTRICITY BY INDUCTION OR INFLUENCE.

A body charged with electricity and brought into the neighbourhood of an insulated conductor in its natural state, produces an immediate separation of the electric fluids in that body, repelling that of the same kind with its own charge, and attracting that of the opposite kind. Thus, let an insulated metallic cylinder  $BC$  (*Fig. 377*), having a number of pith-ball electroscopes suspended from it, be brought near a body  $A$ , charged

*Fig. 377.*



with  $+E$ , but not near enough to allow a spark to pass between them. The electroscopes near the extremities of the cylinder will immediately diverge, while those near the middle keep their natural position. On the removal of the charged ball, they all fall down again, and resume their divergent position when it again approaches the cylinder. Further, if a pith-ball suspended on silk and charged with  $+E$ , be held near different parts of the cylinder while the ball  $A$  is in position, it will be attracted at the end nearest to  $A$ , repelled at the farther end, and neither attracted nor repelled near the middle, showing that the near end exhibits electricity opposite to that of  $A$ , and the farther end the same electricity as  $A$ . The same may be further shown by touching the different parts of the cylinder with a proof-plane, and transferring the charges to an electroscope; this mode of testing also shows that there is, somewhere between the extremities of the cylinder, a neutral line, where neither kind of electricity predominates. The exact position of this line and the distribution of the opposite electricities on either side of it varies with the dimensions of the cylinder, its distance from the charged body  $A$ , and the strength of the charge of  $A$ . When the charged body  $A$  is removed, the two electricities in  $BC$  reunite, and this body no longer exhibits any electric excitement, provided always that the two bodies have never been brought near enough to allow of an interchange of their opposite electricities in the form of a spark, and that  $BC$  has remained insulated all the time.

Suppose now that while  $BC$  is under the influence of  $A$ , a second insulated conducting cylinder is joined on to the end  $C$ . The  $+E$  will then be driven into this second cylinder, and the first will exhibit  $-E$  over the greater part of its surface. Now separate the two cylinders, and then remove the body  $A$ . The first cylinder then remains permanently negative and the second positive. Suppose, in the next place, that the cylinder  $BC$ , while under the influence of  $A$ , is touched with the finger. The  $+E$  will then be driven into the ground, the cylinder will remain negative, and if it be again insulated before  $A$  is removed, it will remain permanently negative. This effect may easily be shown by the gold-leaf electroscope. On holding over the cap an excited stick of sealing wax, the  $+E$  of the electroscope is drawn up into the cap, and the  $-E$  driven into the leaves, which then diverge; on removing the sealing wax, the two electricities recombine, and the leaves collapse; but if, while the excited wax is held over the electroscope, the cap be touched with the finger, the leaves collapse, because the  $-E$ , which made them diverge, is driven into the ground; if the finger be then removed, the sealing-wax remaining in position, the leaves will still hang vertically; but on then removing the wax, they instantly diverge with a positive charge, because the positive electricity previously retained in the cap by the attraction of the  $-E$  of the excited wax, now distributes itself uniformly through the cap, wire, and leaves, which



thus acquire a permanent positive charge. On again approaching the excited wax or other negatively electrified body, they collapse; but the approach of an excited glass tube makes them diverge more widely. This is the most convenient way of using the gold-leaf electroscope to see whether the charge of a given body is positive or negative.

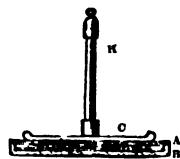
The separation of the electric fluids in a neutral body under the influence of an electrified body is called *electrification by induction or influence*. It is evident that a body charged with either kind of electricity must exert this influence on all the bodies in its neighbourhood, separating their electric fluids with more or less facility, according to their conducting powers. When a light body, such as a feather, is brought near an electrified body, the opposite electricity is developed on the nearer side of the feather, and the mutual attraction of the opposite electricities causes the feather to approach the excited body. The attraction of neutral by charged bodies is, therefore, merely a particular case of the mutual attraction between the opposite electricities.

It is evident that the influence of a charged body on the electric fluids of neighbouring bodies will be exerted equally whether they are previously in their natural state or not. When two bodies similarly charged, say both with  $+E$ , are brought near each other, the mutual repulsion of the similar electricities causes them to accumulate on those points of the surfaces which are farthest from each other. On the other hand, if they are oppositely charged, the mutual attraction of the  $+E$  and  $-E$  causes them to accumulate in greatest quantity on the contiguous portions of the surfaces. When a body containing excess of  $+E$  is brought near a neutral body, as B C (*fig. 377*), the  $-E$  drawn to the nearer end of that body acts upon the  $+E$  of A, causing it to accumulate on the part of A nearest to B; and this again causes a further flow of  $-E$  to B, and thus the action goes on till, if the bodies are not too far apart, the mutual attraction of the opposite electricities is strong enough to overcome the resistance of the air or other intervening insulator, and an interchange of the two takes place in the form of a spark, the result being that the previously electrified body has its charge diminished, and the previously neutral body, if insulated, becomes permanently charged with the same kind of electricity as A.

We proceed to apply the preceding principles to the construction of several useful electrical instruments.

**The Electrophorus.**—This instrument consists of a cake or plate A (*fig. 378*), of some material easily excited by friction, as glass, ebonite, gutta serena, or resinous mixtures of various kinds, resting on a metallic plate B, called the sole, and provided with a metallic cover C, which simply rests upon it, and can be removed by an insulating handle H. A good material for the cake, according to Böttger, is 5 pts. shellac, 5 mastic, 2 Venice turpentine, and 1 marine glue, (a mixture of shellac, coal-tar, and caoutchouc, *i. 739*). This mixture must be carefully heated over a fire, so that when poured out, it may have no air bubbles on its surface. Pfaff recommends a mixture of 8 pts. colophony, 1 shellac, and 1 Venice turpentine. Shellac mixed only with 10 per cent. Venice turpentine is still better, but dearer. Either of these resinous mixtures is better than glass or ebonite, because it does not condense moisture so easily on its surface.

*Fig. 378.*



The resinous cake, when beaten with a cat-skin, becomes negatively electrified. When the cover is laid upon it, no communication of electricity takes place from one to the other, but the  $-E$  on the surface of the cake acts inductively on the electric fluids of the cover, attracting the  $+E$  to the lower surface and repelling the  $-E$  to the upper. If the cover be lifted up by its insulating handle, the electric fluids reunite, and the cover appears perfectly neutral. But if, while it rests on the cake, it be touched with the finger, the  $-E$  on its upper surface is driven away, and more  $+E$  enters it; so that, on removing the finger and then raising the cover by its insulating handle, it appears strongly positive and gives bright sparks. On discharging the cover, replacing it, again touching it with the finger, insulating, and raising it by the handle, it will again be found charged with  $+E$  as strongly as before; and this charging of the cover may be repeated any number of times, as long as the surface of the cake retains its negative charge, which in a dry atmosphere it will do for a long time. Indeed, if the cover be laid on the cake and the apparatus set aside in a dry place, it will retain its charge for months.

If glass, or any other material which becomes positive by friction, be used as the electric, the cover will of course acquire a negative charge.

The electrophorus is a very convenient instrument to the chemist, as it supplies a ready means of obtaining a spark for the explosion of gaseous mixtures.

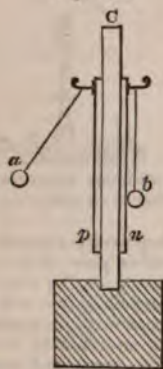
**The Condenser.**—This is a contrivance for increasing the delicacy of electroscopes. On the cover of a gold-leaf electroscope (*fig. 379*) is laid a circular brass plate, well

polished; and on this is laid another brass plate of the same diameter, provided with an insulating handle, and covered on its lower surface with copal varnish, to prevent metallic contact between the plates. Let the lower plate *a*, be connected with a feeble source of electricity (say  $+E$ ) not strong enough to produce a sensible deflection of the gold-leaves. Now touch the upper plate *b* with the finger. The  $+E$  in *a* will then decompose the electric fluid in *b*, driving the  $+E$  away, and causing a

Fig. 379.



Fig. 380.



flow of  $-E$  to the lower surface of *b*; this  $-E$  will then draw more  $+E$  into *a*, and this again will draw more  $-E$  to the lower surface of *b*, and thus the action will go on till a quantity of  $+E$  is accumulated on *a*, much larger than it would otherwise have acquired. Now disconnect *a* with the source of electricity, and lift up the plate *b*. The  $+E$  accumulated on *a* will then diffuse itself through the electroscope, and cause the leaves to diverge. In this way, decided indications of electric action may often be obtained from sources too feeble to produce a deflection of the electroscope by direct communication. Instead of using the instrument in the way just described, the upper plate may be connected with the source of electricity and the lower plate with the ground; in this case, the action will take place in a similar manner, but the electricity with which the leaves diverge will be of the opposite kind to that of the source.

**The Coated Plate and Leyden Jar.**—Let a glass plate *C* (fig. 380) coated on both sides with tin-foil to within about 2 inches of its edges, and having a pith-ball suspended by a thin silver wire attached to each coating, be placed near the conductor of an electrical machine, so that  $+E$  may be communicated to one of its coatings *p*, while the other *n*, remains insulated. Both the pith-balls immediately stand out, and the approach of an excited glass rod shows that *b* as well as *a* has received a positive charge. The cause of this is obvious. The  $+E$  communicated to the coating *p* from the machine draws the  $-E$  of the opposite coating *n* towards the surface of the glass, and repels the  $+E$  to the outer surface of *n*, and into the ball *b*. While the coating *n* remains insulated,  $+E$  continues to flow into the coating *p*, till a particle of it is repelled as strongly in one direction by the action of the  $+E$  on the two coatings *p*, *n*, as it is urged in the contrary direction by the  $+E$  in the conductor of the machine. When this point is attained, the electricity begins to start out from the edges of the coating *p* in sparks and streams in all directions. Now connect *n* with the ground. Immediately the state of tension of the electricity on *p* appears relieved, and the escape of electricity from its edges ceases; in fact the  $+E$  on the outer surface of *n* has been driven away into the ground, and  $-E$  has entered in its place; this  $-E$  draws the  $+E$  on *p* more towards the surface of the

glass, and enables more  $+E$  to enter it from the machine; and this action will go on till a particle of  $+E$  about to enter *p* is as much repelled by the  $+E$  which has already entered *p*, as it is attracted by the  $-E$  on the opposite coating *n*, and repelled by the  $+E$  in the conductor of the machine. During all this time, the coating *p* remains active towards external bodies, giving sparks when touched, and causing the ball *a* to stand out, while *n* remains neutral to external bodies, although it contains a large excess of  $-E$ . This must indeed be the case; for so long as *n* remains uninsulated,  $+E$  will flow out of it, till a particle on the outer surface is as much attracted by the  $-E$  on the rest of the coating *n*, as it is repelled by the  $+E$  on *p*. Further, it is evident that to produce this equilibrium on *n*, the quantity of  $+E$  on *p* must be absolutely greater than that of the  $-E$  on *n*, because the former acts at a greater distance on any particle of electricity in *n*. But from this it also follows that the coating *p* must contain free  $+E$ ; because the  $-E$  on *n*, being smaller in quantity than the  $+E$  on *p*, and likewise acting at a greater distance, cannot

neutralise the whole of it. Hence on removing the apparatus from the machine, and disconnecting  $n$  with the earth,  $p$  appears active, giving sparks and repelling the ball  $a$ , while  $n$  is neutral and the ball  $b$  hangs vertically. Now touch  $p$  with the finger or any other uninsulated conductor; immediately  $p$  becomes neutral, for the same reason that  $n$  was neutral before, that is to say,  $+E$  is driven out of it, till the action of the  $+E$  still remaining on it is neutralised by the  $-E$  on  $n$ . Then, as before, it follows that the quantity of this  $-E$  must now be greater than that of the  $+E$  on  $p$ ; consequently, a portion of the  $-E$  on  $n$  will be free, the pith-ball  $b$  will stand out, and the coating  $n$  will give a spark to any conductor which approaches it. In this way, each coating may be alternately rendered neutral and active, a certain portion of  $+E$  being each time taken from the one, and  $-E$  from the other, till both are restored to their natural state.

The accumulating power of the coated plate may be approximately estimated as follows:

Let the quantity of  $+E$  which the coating  $p$  can take up, when  $n$  is insulated, be denoted by 1; and suppose the thickness of the plate to be such that this quantity 1 on  $p$  can neutralise on  $n$  a quantity of  $-E$  denoted by  $\mu$ , a fraction less than 1. Then  $\mu$  on  $n$  will neutralise  $\mu^2$  on  $p$ ; this will neutralise  $\mu^3$  on  $n$ , and so on. Consequently, the total quantity of  $+E$  accumulated on  $p$  when  $n$  is uninsulated and the plate is fully charged, will be:

$$1 + \mu^2 + \mu^4 + \mu^6 + \&c. = \frac{1}{1 - \mu^2};$$

and the quantity of  $-E$  accumulated at the same time on  $n$  will be:

$$\mu + \mu^3 + \mu^5 + \mu^7 + \&c. = \frac{\mu}{1 - \mu^2}$$

If, for example,  $\mu = \frac{9}{10}$ , the quantity of  $+E$  accumulated on  $p$  will be  $\frac{100}{19} = 5\frac{5}{19}$  and that of  $-E$  on  $n$  will be  $\frac{90}{19} = 4\frac{14}{19}$ ; that is to say, the plate with one coating un-

insulated can take up rather more than 5 times as much electricity as when both sides are uninsulated.

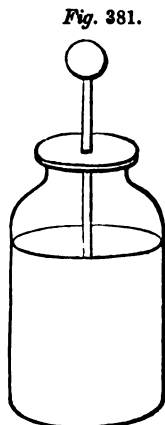
The quantities of  $+E$  removed by alternately touching the two coatings are, from the positive coating,  $1, \mu^2, \mu^4, \mu^6, \&c.$ , and from the negative coating,  $\mu, \mu^3, \mu^5, \&c.$

If, instead of touching the coatings alternately, a direct communication be made between them by touching the neutral coating with a wire and bending it round till it comes within a short distance of the active coating, a sudden discharge takes place, accompanied by a bright flash and a loud snap, the large quantities of the opposite electricities accumulated on the two coatings recombining at once through the conducting wire. The discharge thus effected is not, however, quite complete; a small quantity of electricity always remains, and may be discharged by again connecting the coatings after a short time. This residual charge is due, partly to the penetration of the opposite electricities within the substance of the glass, partly to their extension beyond the edge of the coatings.

When the communication is made by touching the two coatings with the hands, the peculiar convulsive sensation called the electric shock, is experienced in the arms and chest.

The quantity of electricity which may be accumulated on a coated plate of glass or other insulator increases directly with the extent of coated surface. With a given extent of surface, it is also greater as the glass is thinner: for, as the accumulation depends upon the mutual attraction of the opposite electricities on the two surfaces, it will be greater as the distance between them is less. The thickness cannot however be diminished beyond a certain limit, as the two electricities would then recombine through the substance of the glass and cause a fracture.

The charging of a coated insulator takes place in the same way, whatever may be its shape. The most convenient form is that of a glass jar (*fig. 381*) coated with tin-foil inside and out to within a few inches of its lip, and fitted with a wooden lid, through which there passes a brass rod, terminated above by a knob and below by a chain reaching to the bottom. The jar is charged by holding



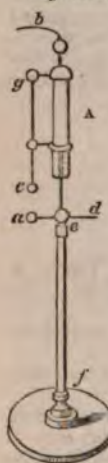


its knob to the conductor of the machine. If it be insulated, sparks may be taken from the outer coating all the time that the charging is going on. In this way two jars may be charged at once; but, from the preceding explanation, it is evident that the charge of the second jar will not be so strong as that of the first.

When a very large extent of coated surface is required, a number of jars are connected together by placing them in a tray lined with tin-foil and joining their knobs by brass rods; they then act as one jar. The arrangement is called an *Electrical Battery*.

*Unit-jar.*—This is a very useful contrivance, invented by Mr. Harris, of Plymouth, for measuring the quantity of electricity communicated to a large jar or battery. It consists of a small Leyden jar, A (*fig.* 382), supported in an inverted position on the insulating stem, *ef*. The inner coating of this jar is connected by the wire *ad* with the positive conductor of an electrical machine, and its outer coating is connected by

*Fig.* 382.



the wire *b* with the inside coating of the jar or battery to be charged. To the outer coating of A there is also attached a wire *gc*, terminating in the brass knob *c*, at a short distance from *a*. On working the machine,  $+E$  is communicated to the inside of the unit-jar A, and a certain quantity of  $+E$  is thereby driven from the outer coating through the wire *b* into the jar or battery to be charged. As soon, however, as the charge of the unit-jar, has reached a certain degree of intensity, a discharge takes place by a spark, between the knobs *a*, *c*, this discharge merely neutralising the charge of the unit-jar, without affecting that of the large jar or battery; on continuing to work the machine, more  $+E$  is driven from the outside of A into the large jar, and, after a while, the small jar is again discharged by a spark at *a*, *c*. Now, as the distance of the knobs *a*, *c* remains constant, it is clear that each discharge indicates an equal charge of the unit-jar, and consequently the transference of an equal quantity of  $+E$  from the outside of this jar to the inside of the larger jar or battery. Hence the number of sparks passing between the knobs *a*, *c* serves as a measure of the quantity of electricity accumulated in the large jar or battery.

#### THE ELECTRIC DISCHARGE.

The recombination of the opposite electricities which constitutes discharge, may, as already observed, be either continuous or sudden,—continuous, or in the form of a current, when two sources of the opposite electricities are connected by a good conducting chain,—as when the two conductors of a cylinder machine (*p.* 379) are joined by a metallic chain or wire;—sudden, when the opposite electricities are allowed to accumulate on the surfaces of two contiguous conductors till their mutual attraction becomes strong enough to overcome the intervening resistances, whatever they may be. It is scarcely necessary to observe that the difference here mentioned is one, not of kind, but of degree; there is no such thing as an absolute non-conductor, and the very best conductors, viz. the metals, offer an appreciable and measurable resistance to the passage of the electric fluid; still the difference at the two extremes of the scale is sufficiently great to give rise to a wide range of phenomena.

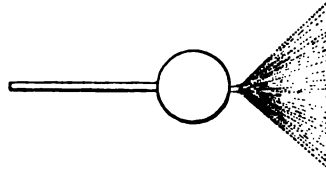
#### *Discharge through Air and other Gases: the Electric Light.*

When two oppositely charged conductors are brought within a certain distance of one another in a gaseous medium, discharge takes place between them in the well-known form of the electric spark. The form, dimensions, brightness, and colour of the spark, vary considerably according to the size and shape of the conductors, and the nature and physical state of the surrounding medium. When the surfaces are well rounded, as those of spheres, or the ends of cylinders of considerable diameter, and the distance between them not very great, the sparks are nearly continuous, straight, and attended with a loud snapping noise; on increasing the distance, they pass at longer intervals, and with a louder noise, because the opposite electricities have to be brought to a higher state of tension before they can overcome the resistance of the intervening air, and consequently a greater quantity of electricity passes in a single spark. At a still longer interval, if the machine is in good action, the sparks become forked, as if the electricity were seeking out the easiest passage through the air, and taking advantage of any conducting matter, such as particles of dust, that may be floating in it; at the same time the spark becomes less bright, and is attended with a duller snap and more or less of a sputtering noise. Between smaller balls, or when a small ball is presented towards the conductor of the machine, the sparks at a given distance are more con-

tinuous, because a smaller quantity of electricity suffices to produce the requisite tension.

When a brass rod terminating in a ball is inserted into the positive conductor of a machine in good action, and no other good conductor is near, the electricity is often discharged from it in the form of a brush (*fig. 383*), consisting of a short straight stem and numerous diverging ramifications, the effect being greatly assisted by any slight roughness on the surface of the ball, or by holding a large conducting surface, such as the hand, at the distance of a few inches from it. It is caused by the discharge of comparatively small quantities of electricity at very short intervals, the tension at one point of the electrified ball being brought up to the discharging point, while there is no good conductor near enough to receive a larger quantity of the accumulated electricity at once. The electricity then escapes into the air in visible streams, the light becoming fainter and fainter as it is diffused over a wider space, and at a certain distance ceasing altogether. A large conducting surface held within a certain distance of the ball facilitates the brush discharge, by itself assuming the negative state of charge, and thus intensifying the positive charge on the ball (*p. 385*).

Fig. 383.



By using a smaller ball or a thick wire with a rounded end, the brush becomes more continuous, but smaller and less luminous, and when the conductor terminates in a sharp point, the brush disappears altogether, and is replaced by a quiet and continuous glow, surrounding the point, and accompanied by a stream of air flowing outwards from it. In this case, in consequence of the intensity of the charge near the end of the wire, the surrounding particles of air are quickly brought into a similar electrical state, and are repelled, and thus carry away the electricity of the pointed conductor so rapidly, that only a small quantity of it escapes in visible form. The glow may be changed into a brush by anything which impedes the current of air, as by the approach of the hand or other large conducting surface. The glow is of a more continuous character than the brush, a smaller quantity of electricity sufficing to keep the end of a pointed wire at the discharging tension than when the conductor has a rounded termination. Hence glow may be changed to brush by charging the conductor at intervals instead of continuously; thus a pointed wire inserted into an insulated conductor placed in contact with the conductor of an electrical machine, will exhibit glow discharge; but by separating the two conductors, so that sparks may pass from the machine, the glow is changed into a succession of brushes.

The character of the brush in air varies greatly according as the body from which it proceeds is electrified positively or negatively. The negative brush (*fig. 384*) is in all cases much smaller and more compressed than the positive brush, never exhibiting the same beautiful ramifications as the latter. This is the case whether the negative brush proceeds from a small knob or a blunt-pointed rod inserted into the negative conductor of the machine, or from a similar knob or wire held within a certain distance of the positive conductor, so that it may acquire a negative charge by induction. When the two brushes are produced simultaneously, by holding an uninsulated knob or wire near another wire inserted into the positive conductor of the machine, the difference in their appearance is very conspicuous (*fig. 385*).

Fig. 384.

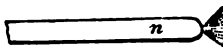
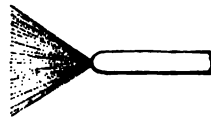
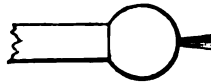


Fig. 385.



The cause of this remarkable difference has been the subject of much discussion, and is perhaps not quite satisfactorily made out; but it is most probably related to the fact, which Faraday has demonstrated by numerous experiments (*Experimental Researches*, series xii. xiii.), that negative electricity discharges into air at a somewhat lower tension than positive electricity, so that a negatively electrified knob or wire projecting into the air is sooner brought up to the state of tension at which discharge commences, than one which is positively electrified, and therefore discharges the electricity at shorter intervals and in smaller quantities at once. Faraday has ascertained that a rounded metal rod projecting into the air and electrified negatively, discharges at intervals seven or eight times shorter than when it is charged positively. In



accordance with this, it is found that the approach of the hand, or other large conductor, does not alter the character of the negative as it does that of the positive brush, until it is brought near enough to produce a spark.

When the end of the electrified conductor is reduced to a point, very little difference can be perceived between the positive and negative discharge from it.

*Dark Discharge.*—The glow discharge, especially on a negative surface, is generally accompanied by a dark interval through which the electricity appears to travel without being visible. Faraday describes an experiment in which two brass rods 0.3 of an inch in diameter, entering a glass globe on opposite sides, had their ends brought in contact, and the air about them very much rarefied. A discharge of electricity was then made through them, and whilst that was continued, the ends were separated one from the other. At the moment of separation, a continuous glow came over the negative rod, the positive termination remaining quite dark. As the distance was increased, a purple stream or haze appeared on the end of the positive rod, and proceeded directly outwards to the negative rod, elongating as the interval was enlarged, but never joining the negative glow, there being always an interval of  $\frac{1}{18}$  to  $\frac{1}{20}$  of an inch between them. The appearance is shown in fig. 386.

Fig. 386.



It appears then that air can discharge electricity, like a conductor, without luminosity. In many cases, the effect is doubtless to be attributed to the current of air which, as already observed, invariably accompanies glow; in other cases, however, this explanation will scarcely suffice: for dark intervals are often seen in sparks, especially in coal-gas, in which case the discharge is too rapid to admit of the formation of a current of air. In such cases, the dark intervals probably consist of portions of air possessed of greater conducting power than the rest, perhaps from the presence of particles of dust—or in coal-gas, in which they are peculiarly conspicuous, from the presence of minute particles of solid hydrocarbons floating in the gas. The phenomenon may be compared to that which is seen in the ignition of a wire composed of alternations of silver and platinum by the voltaic current, the silver, which conducts better than the platinum, appearing less luminous.

*Discharge in Rarefied Air.*—When the air between two oppositely charged bodies is rarefied, the number of particles which oppose the union of the opposite electricities is diminished, and consequently a lower intensity of charge will be sufficient to induce their combination. Hence with a given charging power, the spark will strike through longer distances. The most convenient apparatus for showing this effect is an ordinary cylindrical receiver standing on the plate of an air pump, and closed at the top with a brass cap and stuffing box, through which there passes a brass rod, terminating, within the receiver, in a ball, or point, or any other desired form. By connecting this rod with the conductor of the machine, and working the pump, the increased facility of discharge as the rarefaction proceeds is strikingly exhibited. When the exhaustion has been carried to a considerable extent, the whole of the receiver appears filled with beautiful streams of violet or rose-coloured light, which pass with little or no noise.

The conditions which determine the occurrence of brush and glow in highly rarefied air are much the same as in air of ordinary density. When the sliding wire is placed in complete metallic communication with the conductor of the machine, so that the supply of electricity is very regular, the ball at the lower end of the wire generally becomes covered with a quiet glow, the greater part of the receiver remaining dark, and only a few slight coruscations appearing here and there on the plate of the air pump; but by allowing sparks to pass from the machine, the discharge in the receiver immediately takes the forms of splendid streams and brushes. Rarefaction of the air seems to develop the negative brush in a greater degree comparatively, than the positive brush. According to Faraday, extensive ramifications are easily obtained from a ball or rounded termination electrified negatively, to the plate of the air pump. The glow is also very easily produced on a negative ball in rarefied air.

It is of course impossible to say what would take place in a perfect vacuum, whether in fact the discharge would take the form of a continued stream, or be stopped altogether; the former supposition is perhaps the more probable; but in an atmosphere of extreme tenuity, such as the Torricellian vacuum, in which, however, vapour of mercury is present, or the vacuum produced by filling a tube with carbonic acid gas, exhausting as much as possible with the air-pump, and absorbing the remainder by solid potash, very remarkable effects are observed. The discharge, whether from the conductor of an electrical machine, or from a Leyden jar discharged through a wet string, or from a voltaic battery, or from an induction coil, generally exhibits remark-

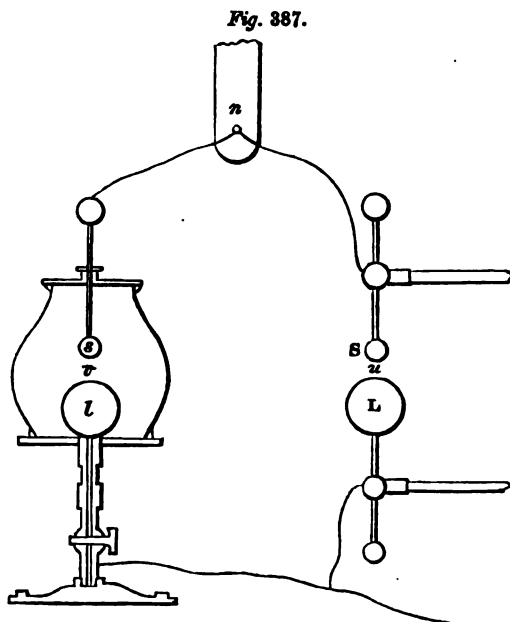


able stratifications, that is, alternations of light and dark bands, extending from one terminal conductor to the other. These stratifications, which have probably some analogy to the light and dark bands observed by Faraday in the spark, and other forms of discharge, are seen only when the rarefaction is carried to a very high degree—but, on the other hand, they disappear when the vacuum is nearly perfect, the discharge then appearing continuous throughout the tube. In the Torricellian vacuum, when not very complete, the discharge is sometimes intensely white, filling the entire tube, without stratification. These curious and brilliant phenomena have been studied in great detail by M. Gassiot, and are described in a series of papers published in the Transactions and Proceedings of the Royal Society (Phil. Trans. 1858, 1859; Proc. Roy. Soc. x. 146, 601; xi. 36, 269, 274, 393, 432). We shall return to them in speaking of the light produced by the voltaic battery and the induction coil.

*Discharge in different Gases.*—Different gases, at the same pressure and temperature, possess different powers

of insulation. Faraday has obtained approximate measures of these differences, by means of the apparatus represented in fig. 387. S, L are two brass balls, the distance between which can be varied at pleasure, and s, l two other balls of nearly the same diameters as S and L, but placed at the fixed distance of 0.62 inch, and enclosed in a receiver which can be exhausted and filled with any required gas. The balls s, S are connected by wires with the insulated conductor n, which can itself be connected at pleasure, either with the positive or with the negative conductor of an electrical machine, and the large balls l, L are connected with the earth.

It is clear that, with air in the receiver, the discharge may be made to pass in sparks either at v or at u, by increasing or diminishing the distance between the balls S, L; and by filling the receiver with different gases, and regulating the distance between these balls, so as to cause all the sparks to pass at v, the relative insulating power of the gases may be measured. It was found, however, that the interval u might be altered within certain limits, and yet sparks pass either there or at v. The extremes were therefore noted, viz. the greatest distance short of that at which the discharge *always* took place at v in the gas, and the least distance short of that at which it *always* took place at u in the air. The intervals were also found to be different according as the small balls s and S were made positive or negative. The following table gives the *mean* results:



	s and S positive.	s and S negative.
Hydrochloric acid gas . . . . .	1.105	0.720
Olefiant gas . . . . .	0.750	0.730
Air . . . . .	0.695	0.635
Carbonic anhydride . . . . .	0.640	0.590
Nitrogen . . . . .	0.615	0.645
Oxygen . . . . .	0.505	0.510
Coal-gas . . . . .	0.490	0.525
Hydrogen . . . . .	0.370	0.275

These numbers show that, with a positive charge on the small balls, and with the same surfaces, and under the same circumstances of pressure and temperature, hydro-

chloric acid gas has three times the insulating or restraining power of hydrogen gas, and nearly twice that of oxygen, nitrogen, or common air. The differences are not due to specific gravity; for though hydrogen is the lowest of all, oxygen is much lower than nitrogen, and also lower than olefiant gas; and carbonic anhydride, though much heavier than olefiant gas or hydrochloric acid, is lower than either. The difference of insulating power in the gases appears, therefore, to be a specific electric quality, or relation (see page 400).

The negative numbers in the preceding table do not follow the same order as the positive numbers. In air, hydrogen, carbonic anhydride, olefiant gas, and hydrochloric acid, the tension rose higher when the smaller ball was made positive than when it was negative, whilst in oxygen, nitrogen, and coal-gas, the reverse was the case. When the conductor *a* was connected only with the receiver containing hydrochloric acid gas, the discharge was found to be easier when the small ball *s* was negative, than when it was positive; in the latter case, much of the electricity was given off as brush discharge from the connecting wire, whereas in the former it all passed through the hydrochloric acid gas.

The colour and appearance of the spark and brush vary considerably according to the nature of the gas.—In *air*, the sparks exhibit the well-known bright light and violet-blue colour, and often have faint or dark parts in their course, when the quantity of electricity passing is not great.—In *nitrogen*, the sparks are very beautiful, having the same general appearance as in air, but more colour of a bluish or purple character.—In *oxygen*, they are whiter than in air or nitrogen, and somewhat less brilliant.—In *hydrogen*, they have a very fine crimson colour, which, however, disappears as the atmosphere is rarefied; the spark in this gas produces very little sound.—In *carbonic anhydride* the colour of the spark is similar to that in air, but with a slight green tint: the sparks are, under similar circumstances, of strength of charge, form of conductors, &c., longer and more regular in form than in air; altogether this gas affords peculiar facility to the spark discharge.—In *hydrochloric acid gas*, the spark is white, and exhibits no dark spaces.—In *coal-gas*, the spark is sometimes green, sometimes red, sometimes partly green and partly red; black parts also occur suddenly in the line of the spark, that is to say, they are not connected by any dull part with bright portions, but the two seem to join directly one with the other.

The appearances of the brush in air have been already described.—*Nitrogen* gives brushes with great facility from positive surfaces; they are always fine in form, light, and colour, and in rarefied nitrogen are magnificent: they surpass the discharges in any other gas, as to the quantity of light evolved. The difference between the positive and negative brushes in nitrogen is greater even than in air.—In *oxygen*, the positive brush is compressed and poor, while the negative brush is not much less developed than in air; indeed, the two are so alike that it is often difficult to distinguish one from the other, and this similarity continues even when the oxygen is gradually rarefied.—In *hydrogen*, the positive brush is more developed than in oxygen, but not so fine as in nitrogen; in rarefied hydrogen, the ramifications are very fine in form, but pale in colour; in the rarest state of the gas they have a pale grey-green tint; the negative brush is much the same in hydrogen as in air.—In *carbonic anhydride*, at common pressures, the positive brush is very poor as to size, light, and colour; in the rarefied gas, it is better in form, but weak as to light, and has a dull greenish or purplish hue; altogether the positive brush in this gas is not much superior to the negative brush.—In *hydrochloric acid gas*, the brush is very difficult to produce at common pressures, even with the interrupted spark-current (p. 389). In the rarefied gas, the brush is more easily formed, but is generally of a low squat form, poor in light, and very similar on the positive and negative surfaces. In the highly rarefied gas, a few large ramifications are obtained from the positive surface, but of a pale bluish colour, utterly unlike those of nitrogen.—In *coal-gas*, the brushes are difficult to produce, as compared with nitrogen, and the positive not much superior to the negative in character, either at common or at low pressures. At common pressures, they are short and strong, generally of a greenish colour, and possessing much of the spark character.

On the whole then it appears that the character of the brush is essentially connected with the nature of the gas through which it passes; that the positive brush always shows a certain degree of superiority to the negative brush; but it is only in nitrogen, hydrogen, and common air that the difference is great, while in oxygen it almost vanishes.

*Glow-discharge* occurs in all the gases above mentioned under circumstances similar to those already described (p. 389); it is always accompanied by a wind proceeding either to or from the glowing part, and if the access of air is interfered with, the glow disappears.

*Dark discharge* has likewise been observed in all the gases examined, most easily in hydrochloric acid, and in coal gas (p. 390). In the latter, the discharge between balls

about an inch apart was accompanied by short brushes on the ends, and a dark interval of about half an inch between them, notwithstanding that the discharge had the quick sound of a dull spark, so that its dark portions could not have depended on convection, that is to say, on the formation of a stream of gaseous particles.

*Luminous Discharge in Liquids and Solids.*—Sparks may be obtained in insulating liquids and solids, as in oil of turpentine, olive oil, resin, glass, &c., their passage being generally attended with more or less disruption of the particles of the body; also in imperfect conductors, such as water, spermaceti, &c. Brushes may be obtained in oil of turpentine, by passing sparks from the machine to a wire going through a glass tube into the liquid contained in a metallic vessel; they are small, and so feebly luminous as to be visible only in a dark room, and exhibit simple, very divergent ramifications. The presence of a few solid particles, as of dust or silk in the liquid greatly facilitates the production of the brush. (Faraday.)

*Duration of the Electric Light.*—Wheatstone has examined the duration of the electric spark by means of a revolving mirror. The principle of the method is this: when a steady light, such as the flame of a candle, is viewed in a fixed mirror, its image appears in one constant direction; but if the plane of the mirror be moved through a certain angle, the image changes its position, and if the mirror be made to rotate very rapidly, the image will appear drawn out into a long line of light, because, in the successive positions through which it passes, it remains for a certain time on the retina, and consequently the luminous impression of the image in its former positions is seen at the same time that it has advanced to a new one. If then the electric spark has any perceptible duration, it must also appear elongated when viewed in a mirror rotating with a certain velocity. In Wheatstone's experiments, the mirror was rotated at a rate which would have produced an elongation of half a degree in the image of the spark, if its duration were equal to  $\frac{1}{75000}$  of a second. No elongation or distortion was, however, perceived in the image of the spark from the conductor of an electrical machine, or from a Leyden jar discharged in the ordinary way, or of the stream of light in an exhausted tube 6 feet long; they all appeared in the rotating mirror just the same as when it was at rest. Under these circumstances, therefore, the duration of the electric spark is less than  $\frac{1}{75000}$  of a second. When, however, the discharge is made through a very long wire, say half a mile long, or through a bad conductor, the image of the spark in the revolving mirror does appear elongated, showing that the discharge is then not momentary but gradual.

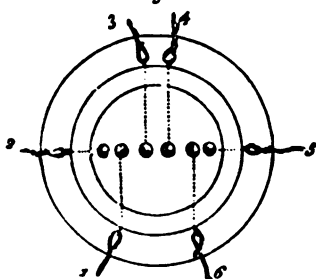
When a rapidly revolving wheel is viewed by ordinary light, its spokes can no longer be distinguished; but when it is viewed by the electric spark in a dark room, the spokes are distinctly seen; in fact, the wheel appears at rest. This likewise shows the momentary character of the ordinary spark. In like manner, a rapidly rotating disc painted with the colours of the spectrum, which appears white by daylight or candlelight, exhibits the separate colours when viewed by the electric spark.

#### *Velocity of the Electric Discharge.*

Wheatstone has applied his revolving mirror to determine the rate at which electricity travels through conductors. For this purpose, six copper balls are fixed on a circular board, called the *spark-board* (fig. 388), and connected in such a manner as to give three sparks with one discharge of a Leyden jar. The wire 1, connects one of these balls with the inside of the jar; from this ball the discharge passes in the form of sparks to the one on the left, and thence through the wire 2, which is joined to 3 by a thin wire  $\frac{1}{4}$  of a mile long, to the third ball; thence, by a spark, to the fourth ball, from which it is conveyed by the wires 4 and 5, also connected by a thin wire  $\frac{1}{4}$  of a mile long, to the fifth ball, and thence by a spark to the sixth ball, which is connected by the wire 6, with the outside coating of the jar. The intervals through which the sparks pass are 0.1 inch wide.

The spark-board is fixed vertically, at a distance of 10 feet from the revolving mirror, and so that the six balls shall be in a horizontal line, parallel to the axis of rotation of the mirror, and at the same height as that axis. The observer places himself so that the axis of rotation is directed towards him, and looks vertically down upon the

Fig. 388.





mirror. The discharging apparatus is arranged so that the sparks may appear just as the mirror is inclined to the horizon at an angle of  $45^\circ$ . (For the details of the arrangement, see De la Rive, ii. 127.)

If, now, the mirror were fixed at this inclination, the three sparks would be seen projected on a horizontal plane, thus : — ; but when the mirror is made to revolve very rapidly, they are all three drawn out into lines : and, moreover, the middle spark appears pushed aside from the others, the relative positions of the three sparks being ——— when the mirror revolves from right to left, and ——— when it revolves

from left to right. From this result Wheatstone deduces the following conclusions :—

1. As the two external sparks retain their relative positions, while the middle one lags behind them, it follows that the discharge begins simultaneously at the two ends of the circuit and proceeds in a perceptible time to the middle.

2. By comparing the observed retardation of the middle spark with the velocity of rotation of the mirror, Wheatstone calculates that electricity travels through a metallic circuit at the rate of 288,000 miles in a second, a velocity greater than that of light (194,000 miles per second), and sufficient to make the circuit of the earth ten times in a second.

Other experimenters, however, by observing the time which the electric current takes to travel through great lengths of telegraph-wires, have obtained results differing widely from that of Wheatstone, and likewise from each other, as the following table will show :—

*Velocity of Electric Discharge.*

Observers.	Nature of Wire.	Miles per Second.
Wheatstone . . . .	Copper . . . . .	288,000
Fizeau and Gonnelle .	Copper (French telegraph)	112,680
Fizeau and Gonnelle .	Iron do.	62,600
O'Mitchell . . . . .	Iron (American telegraph)	28,524
Walker . . . . .	Do. do.	18,780
Gould . . . . .	Do. do.	15,907
Astronomers of Greenwich and Edinburgh . . . .	Copper (London and Edinburgh telegraph)	7,600
Astronomers of Greenwich and Brussels . . . . .	Copper (London and Brussels telegraph)	2,700

The last result is more than a hundred times less than that obtained by Wheatstone.

The cause of these large discrepancies has been pointed out by Faraday (*Experimental Researches*, vol. iii. p. 508), who has shown that when a telegraph wire encased in gutta percha, and buried in earth or immersed in water, is connected with one pole of a voltaic battery, the other pole communicating with the ground, the whole arrangement becomes charged like a Leyden jar, the wire forming the inner coating, the gutta percha the insulator, and the earth or water the outer coating. The inductive action thus exerted necessarily lowers the intensity of the charge in the wire (pp. 386, 387), and consequently the force with which the succession of charges and discharges constituting the current takes place along the wire. Hence the current is retarded, the amount of retardation varying according to the thickness of the gutta percha coating, the conducting power of the wire, and of the medium with which it is surrounded, the perfection of the insulation, &c. The very low velocity obtained with the London and Brussels wire is evidently due to the great conducting power of the water in which a considerable portion of the wire is immersed. A still greater retardation, due perhaps to imperfect insulation, was, however, observed by Faraday, in the subterraneous wire of the London and Manchester line, the current taking two seconds to travel 1500 miles, while, with the same length of wire in air, the time was almost inappreciable. But even with wires suspended in air, a certain amount of retardation is produced by induction towards neighbouring conductors, especially if the wire is stretched close to the ground, or to walls; it must, however, be very small as compared with that which takes place in a subterraneous or subaqueous wire separated from the surrounding conducting medium by an insulating coating only  $\frac{1}{10}$  of an inch thick. In Wheatstone's experiment, the long connecting wires were bent into a number of parallel lengths at

some distance from each other and from the ground; in this case a certain amount of retardation may have arisen from the inductive action of the contiguous portions of the wire on each other; but on the whole, Wheatstone's mode of experimenting probably gives the nearest approximation to the rate at which electricity travels along a copper wire when unimpeded by disturbing causes; but the experiments with the telegraph wires clearly show that no absolute rate can be fixed, the actual velocity varying with the conducting power of the wire or other channel of communication, and the influence of neighbouring bodies.

*Mechanical and Thermic Effects of the Electric Discharge.*

The manner in which electricity travels through a solid body depends upon the relation between the dimensions and conducting power of that solid and the quantity and intensity of the charge. A thick mass of metal, or other good conductor, will convey any charge of electricity, even that of a thunder-cloud, without suffering any visible alteration; but when the charge is sent through thin wires, the result is different. The wire then becomes heated, showing that its particles are thrown into a state of agitation, the degree of heat developed depending upon the relation between the quantity and intensity of the charge and the conducting power of the wire; and when the charge of a powerful battery is transmitted through a very fine wire of silver, gold, copper, zinc, platinum, &c., the metal is melted and disintegrated, with a brilliant flash of light, and if stretched on paper, its particles are driven into the paper, forming an indelible stain.

The degree of heat developed in metallic wires under different circumstances by the discharge of an electrical battery has been investigated by Riess by means of an apparatus called an *electrical air thermometer*, originally invented by Harris. It consists of a glass globe (*fig. 389*) about 3 inches in diameter, having two lateral openings closed by brass caps, between which is stretched a thin spiral of platinum wire. A cylindrical glass tube about half a line in diameter, sealed to the globe, contains a column of coloured liquid, and serves as the stem of the thermometer, of which the globe is the bulb. When an electric charge is sent through the platinum wire, it becomes heated, and expands the air in the globe; the column of liquid is then pushed outwards, and the expansion indicated by a scale attached to the stem, serves as a measure of the rise of temperature produced in the wire by the discharge.

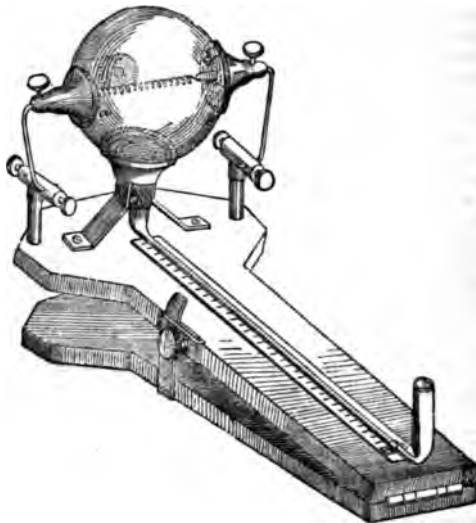
The charge of electricity communicated to the battery is measured by a unit jar. By this mode of observation, Riess has established the following laws:—

1. *The heating of the wire is directly proportional to the square of the quantity of electricity, and inversely proportional to the coated surface over which it is diffused (or directly proportional to the intensity); or if  $h$  be the rise of temperature measured by the expansion of the air in the thermometer,  $q$  the quantity of electricity, and  $s$  the extent of coated surface,*

$$h = n \frac{q^2}{s},$$

$n$  being a constant depending on the thickness and length of the platinum wire and the rest of the conducting circuit. This law may be illustrated by the numbers in the following table, which contains the results of some of Riess's experiments. The

*Fig. 389.*



numbers in the uppermost horizontal line denote the number of jars of the same size composing the battery:—

<i>s</i>	2	4	6
<i>q</i>	<i>h</i>	<i>h</i>	<i>h</i>
2	1.5		
4	6.7	3.2	2.6
6	13.4	7.3	5.5
8	.	14.1	9.3

2. *The rise of temperature produced by a given discharge in wires of the same metal of equal length, but different diameter, is inversely as the fourth powers of their diameters, and the quantities of heat evolved are inversely as the transverse sections of the wires.* Thus, in wires whose diameters are as 1, 2, 3, &c., the same discharge produces rises of temperature which are as 1,  $\frac{1}{16}$ ,  $\frac{1}{27}$ , &c.; but, as the masses of the wires are as 1, 4, 9, it is clear that the quantities of heat evolved in them must be as 1,  $\frac{1}{4}$ ,  $\frac{1}{9}$ , &c., that is, inversely as the transverse sections.

3. *With the same wire in the thermometer-bulb, the rise of the temperature produced in it by discharge of a given quantity of electricity, is less, the longer the circuit through which the discharge has to pass, and the thinner the wires that are inserted into it; in other words, the rise of temperature produced by the discharge of a given quantity of electricity diminishes as the conducting power of the circuit is less.*

Wires of different metals of the same length and thickness inserted into the circuit, produce different degrees of diminution of the heat evolved in the thin wire: thus a platinum wire produces 6.44 times as much diminution as a copper wire of the same length and thickness: hence it is inferred that platinum offers 6.44 times as much resistance as copper to the passage of electricity.

The melting of very thin wires by the electric discharge is not a consequence of the heat evolved, but a specific electrical effect. For, by calculations founded on the observed rise of temperature produced in thicker wires, Riess has shown that the rise of temperature produced in a platinum wire, by a discharge strong enough to melt it, does not exceed 211° C.,—a heat not sufficient even to raise it to redness, much less to fuse it. And in fact, on sending through such a wire charges not quite sufficient to ignite it, appearances are observed which indicate a violent mechanical disturbance of its particles. The wire is sensibly agitated; small sparks appear at its extremities; particles are thrown off from its surface, in the form of a dense vapour; and the wire, if not tightly stretched, becomes bent in several parts, the number and sharpness of the flexures increasing with the strength of the charge; finally, with a certain strength of charge, the wire becomes red or white hot, and its particles are completely scattered. Easily oxidable metals, like iron, burn at the same time in the air, and are partly melted by the heat of the combustion.

Bodies of small conducting power are variously affected by the electric discharge. Electricity of low intensity cannot force its way suddenly through an imperfect conductor, even though the quantity accumulated, in a large battery, for example, may be very considerable. When a jar or battery is discharged through an imperfect conductor, such as wood, the discharge occupies a perceptible time, as may be known by the sound produced. When the resistance of the intervening solid body is very great, as that of glass or shellac, the accumulated electricity is dissipated in the air, sooner than it can pass through the non-conducting solid. But electricity of high intensity forces its way through bad conductors, often tearing them asunder and shattering whatever comes in its way. When two pointed wires are inserted into the ends of a piece of dry wood, and the charge of a large jar or battery sent through them, the wood is torn in pieces. In like manner, card-board, glass, thin cakes of resin, &c. may be perforated. Leyden jars are sometimes destroyed by the electricity of a strong charge forcing its way through the glass from the inner to the outer coating: a round hole is thereby produced, filled with finely powdered glass. When a powerful charge from a battery is sent through a piece of sugar placed between two wires, the sugar is broken into several pieces, which are thrown violently about, and appear phosphorescent in the dark for several minutes; this last effect shows clearly the violent agitation to which the molecules of a body are subjected by the passage of electricity. The destructive effects of lightning, when it strikes a stone or wooden building, or the mast of a ship, not provided with a metallic conductor, belong to the same class of phenomena.



*Chemical Effects of the Electric Discharge.*

The highest charge of electricity, while remaining quiescent in a body, or in the statical condition, produces no perceptible change in its chemical constitution; but electricity in the state of discharge, or in the dynamic state, is capable of inducing both combination and decomposition.

Inflammable bodies are often set on fire by the electric discharge. The discharge of a moderate-sized jar instantly inflames a mass of tow filled with pounded resin. The spark from a very powerful electrical machine produces the same effect, and also sets fire to deal-shavings. A very small electric spark passed through a mixture of hydrogen, carbonic oxide, alcohol-vapour, ether-vapour, &c., with air or oxygen, or a mixture of chlorine and hydrogen, causes instant combination, attended with violent explosion if the gases are mixed in the combining proportions. Whether this effect is due to the heat developed by the spark, or to a direct exaltation of the chemical affinities concerned, is not precisely known, but the latter supposition is perhaps the more probable of the two. (For the methods of inflaming gaseous mixtures by the electric spark in analysis, see *ANALYSIS, VOLUMETRIC, OF GASES*, i. 269.)

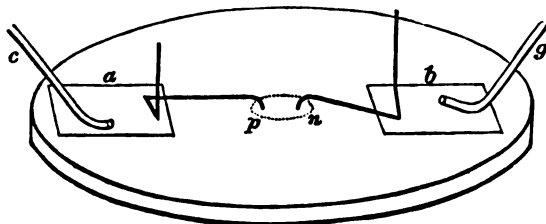
The passage of electric sparks through moist air is always attended with the production of nitric acid: hence this acid is always present in the air after a thunder-storm. (See *NITRIC ACID*.)

Another very remarkable chemical effect of the electric discharge through air or oxygen is the formation of ozone. The air in the neighbourhood of an electrical machine in action always acquires a peculiar pungent odour, somewhat like that of phosphorus slowly oxidising; at the same time it acquires increased oxidising power, decomposing iodide of potassium, decolorising tincture of guaiacum, &c. These effects, first observed by Van Marum in the latter part of the last century, and since more particularly studied by Schönbein and others, are attributed by some to the production of an allotropic modification of oxygen, by others to the formation of a higher oxide of hydrogen ( $H^*O^*$ ). That the effect is due, in great part at least, to a peculiar modification of oxygen, is completely proved by the fact that perfectly pure and dry oxygen acquires this exalted power when electric sparks are passed through it, or along the outside of a sealed tube containing it. Whether, when water is present, a higher oxide of hydrogen is likewise formed, is a question still under discussion. (See *OZONE*.)

Gunpowder laid on a plate of glass between the ends of two wires, may be fired by the discharge of a jar retarded by passing through a wet string or other imperfect conductor; without such retardation, the discharge merely scatters the powder, without firing it.

When a considerable quantity of electricity is passed gradually, and without formation of sparks, through a compound liquid, that liquid is in many instances resolved into its elements, which separate in opposite directions, the one taking the direction of the positive, the other that of the negative electricity. This effect is called *ELECTROLYSIS*, that is, decomposition by electricity. We shall consider it more fully hereafter, merely describing at present the methods devised by Faraday for showing that chemical decomposition can be produced by friction electricity. A glass plate (*fig. 390*) has two strips of tin-foil *a*, *b* pasted on it; one of these is connected by a wire *c*, or wire and wet string, with the positive conductor of an electrical machine, the other by a wire *g* with the earth or the negative conductor. A small piece of filtering paper moistened with the liquid to be decomposed is laid on the plate midway between the two strips of tin-foil, and connected therewith by bent platinum-wires, as shown in the figure. Positive electricity then enters the solution at the point *p*,

Fig. 390.

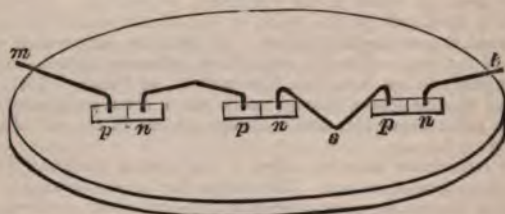


and negative electricity at *n*. Now let the paper be moistened with a solution of iodide of potassium, and the machine worked. In a short time a brown spot of iodine will be produced at *p*, while no apparent change takes place at *n*; but if the

current be reversed by connecting *c* with the positive, and *g* with the negative conductor, a spot of iodine will soon appear at *n*, while that at *p* will disappear. If a piece of paper moistened with hydrochloric acid and coloured with indigo, be placed between *p* and *n*, the paper will be bleached at *p*, indicating the evolution of chlorine. When a piece of litmus paper is placed under *p*, and turmeric paper under *n*, both being moistened with sulphate or chloride of sodium, and the two made to touch each other, a red spot appears under each terminal, showing that an acid has been evolved at *p*, and an alkali at *n*. In a similar manner many other decompositions may be effected.

By the arrangement shown in *fig. 391*, several portions of the same solution or of

*Fig. 391*



different solutions may be decomposed at once, the acid or chlorous elements being always evolved at the positive terminals *p*, and the basic elements at the negative terminals *n*.

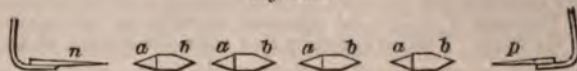
Instead of using the continuous current of the machine, the charge of a jar may be passed through the arrangement, a piece of wet string about four feet long being interposed in the circuit, to retard the discharge; the same decompositions are then produced. Without the interposition of the wet string, however, no decomposition takes place: it seems therefore to require a certain time. The greater the quantity of electricity passed, the greater also is the amount of decomposition produced.

The mode of passing the electricity through the solutions may also be varied in other ways, the only necessary condition being that a continuous current shall pass. Thus, if two triangular pieces of litmus and turmeric paper (*fig. 392*) moistened with

*Fig. 392.*



*Fig. 393.*



sulphate of sodium be placed between two metallic points *p*, *n*, connected with the conductors of an electrical machine in action, the turmeric paper being towards the negative, and the litmus *b* towards the positive terminal, the extremities of both papers will be reddened. This effect may also be repeated through several alternations, as in *fig. 393*, the pointed pieces of moistened paper serving to discharge the electricity like pointed wires.

In all these experiments, especial care must be taken that no sparks pass through the air over the moistened papers; for the passage of a spark through the air always gives rise to the formation of nitric acid, and this would of itself redden litmus, prevent the reddening of turmeric by an alkali, and separate iodine from iodide of potassium.

#### *Magnetic Effects of the Electric Discharge.*

When a piece of unmagnetised steel wire is placed at right angles to a wire of any metal, or to any conductor whatever, through which the charge of a large battery is

passed, the steel wire is rendered permanently magnetic, the direction of its poles being determined by a law which will be hereafter explained. If the steel needle be placed in the axis of a glass tube round which a helix of copper wire is coiled, and the charge, even of a small jar, be sent through the helix, the steel will also be permanently magnetised. The helix serves to intensify the action, by enabling the current to act upon all parts of the steel wire at once. This development of magnetism in steel is produced by the sudden discharge of electricity through good conductors in the neighbourhood of the steel.

The sudden discharge does not, however, produce any *deflection* of a magnetic needle; this requires time, or the action of a continuous current. That friction electricity is capable of deflecting the magnetic needle in the same manner as voltaic electricity, was first shown by Colladon of Geneva, whose results have been fully confirmed by Faraday. When the charge of a powerful battery is made to pass through the coil of a galvanometer consisting of copper wire covered with silk, the velocity of the discharge being diminished by interposing a wet string in the circuit, the needle is immediately deflected, its direction being determined by that of the current, in exactly the same manner as by the current of the voltaic battery. The deflection may also be produced by the direct current of the machine. For this purpose, one extremity of the galvanometer coil is connected with the negative conductor, and the other with a discharging rod, either by a wire or by a wet string. The machine is then worked, and the knob of the discharging rod brought in contact with the positive conductor of the machine. The needle immediately moves a little; as it begins to swing back, the contact with the machine is to be broken; then, when the needle has completed its backward swing, and is about to return, the circuit is again to be completed. In this manner, a fresh impulse is given to the needle, which, added to the first, makes it swing through a larger arc, and by repeating this mode of proceeding several times, the needle may be deflected  $30^{\circ}$  or  $40^{\circ}$ .

#### *Molecular Theory of Electric Action.*

We have hitherto regarded the phenomena of electricity as resulting from the mutual action of two fluids (or two modifications of the same fluid), which are capable of passing through ponderable bodies and from one body to another, and whose particles attract and repel one another with forces varying inversely as the squares of the distances between them. The preceding expositions are perhaps sufficient to show that this theory affords a connected view of all the leading phenomena of electricity as developed by friction.

Faraday, however, has proposed a totally different theory, which he has developed in the eleventh, twelfth, and thirteenth series of his "Experimental Researches." According to this theory, electric action is supposed to take place, not at finite distances, but solely between contiguous particles of matter. A body charged with either electricity, say with  $+E$ , exerts a polarising action on those particles of the air, or other insulating medium, with which it is immediately in contact, inducing the opposite polarity ( $-E$ ) on their nearer ends, and the polarity similar to its own ( $+E$ ) on their farther ends; these particles thus polarised act in like manner on those immediately beyond them, those again on the next, and so on, the action continually extending outwards in all directions through the insulating medium, or dielectric, and the intensity of the charge becoming less, as it is communicated to a wider range of particles. If a conducting body is interposed in the sphere of action, its particles also become polarised, exactly in the same manner as those of the dielectric, the difference between insulators or dielectrics and conductors consisting in this, that the particles of a conductor are easily brought into the charged or polarised state by the influence of an electrified body, but immediately return to their ordinary unpolarised state as soon as that influence is removed,—whereas, those of an insulator offer considerable resistance to the polarising action of an electrified body, but when once polarised, return but slowly to their ordinary state, after the removal of the disturbing cause. This difference is, of course, one of degree only, not of kind, the best conductors offering some resistance to the polarising or inductive action, and the best insulators losing their polarised condition after a certain time.

Such, according to Faraday, is the process by which a body or medium becomes electrically charged by the inductive action or influence of a previously electrified body. Discharge is the return of the whole system of charged particles to their natural or uncharged state, and takes place when one particle, or a certain number of particles, in the system, is raised by the joint action of all the forces concerned, to a state of tension which it is unable to bear: in that case, this particle or set of particles first gives way, and all the rest follow; the system, in the charged state, is, in fact, in a condition of unstable equilibrium, and gives way at its weakest point, the return to



the state of stable equilibrium taking place with more or less violence, according to the nature of the particles concerned, and the intensity of their previous polarisation. The spark or other visible manifestation of electric action, marks the line of particles along which the greatest intensity of action takes place.

This molecular view of electric action is based upon the following facts and considerations:—

1. *The phenomena of electric discharge in gases and other insulating media vary according to the nature of the medium, which must therefore be directly concerned in their production.*

That the insulating medium intervening between charged conductors has something to do with the phenomena of charge and discharge, beyond acting as a mere obstacle to the union or neutralisation of the opposite electricities, is sufficiently proved by the different insulating powers of gases, at the same pressure and temperature; by the appearance and mode of formation of the spark and brush, and the very different characters of these forms of discharge in different gases; further by the effects produced by the electric discharge on solids and liquids (pp. 396, 397).

These phenomena, however, are not in themselves sufficient to show that the polarisation of the individual particles of a body or medium is the main thing in electric action, and that it is by the successive polarisation of such particles, and not by a direct action at a distance, that the influence of a charged body is conveyed to neighbouring conductors. The facts on which the molecular view is chiefly based are the following:

2. *Every dielectric medium exerts a certain influence, peculiar to itself, on the degree of electric induction which takes place through it; in other words, every such medium has a specific inductive capacity.*

To explain the meaning of this, suppose an electrified plate of metal, A, to be suspended midway between two similar plates, B, C, and exactly parallel to them. Then, if there is nothing but air between them, the plate A will induce equally towards B and C; but on interposing any other medium, say shellac, between A and C, the inductive actions exerted by A on B and C will no longer be equal. For the description of the apparatus and mode of experimenting, by which this question has been investigated, we must refer to Faraday's eleventh series of "Experimental Researches," or to the works of De la Rive and Riess; but the principle of the method may be explained as follows:

Suppose we have two Leyden jars with equal extent of coated surface, equal thickness of glass, and in short equal and similar in every respect. Charge one of them in the ordinary way to such a degree, that the charge, when communicated to an electrometer, shall exhibit a repulsive force, say of  $40^\circ$ ; then divide the charge between the two jars, by making a communication between the outer coatings, and bringing the knobs in contact. The charge will of course be equally divided between them, so that, if no loss of electricity has taken place by dispersion, each will exhibit a repulsive force of  $20^\circ$ . Now suppose one of the jars to be made of shellac of the same thickness as the glass, and otherwise similar in every respect. In that case, Faraday finds that the charge is not equally divided between the two; but that if the glass jar is charged first, it loses by communication a greater amount of repulsive force (or intensity) than the shellac jar gains; and on the contrary, if the shellac jar is charged first, it loses by communication a smaller amount of repulsive force than that which is gained by the glass. In short, the shellac acts just like glass of less thickness, a given thickness of it producing a more complete neutralisation of the opposite electricities, a result which is supposed to indicate a higher degree of susceptibility in its particles to inductive or polarising action. This is what is meant by saying that the shellac has greater specific inductive capacity than the glass. The division of an electric charge between two bodies of different specific inductive capacity may be compared with the communication of heat between two bodies of different specific heat, such as water and mercury, the temperature of the one always falling in greater proportion than that of the other rises.

By a method founded on the principle just explained, but not capable of yielding more than very rough numerical approximations, Faraday has obtained the following values of the specific inductive capacities of certain dielectrics:

Air and all other gases . . . . .	1.00
Glass . . . . .	1.76
Shellac . . . . .	2.00
Sulphur . . . . .	2.24

Certain non-conducting liquids, such as oil of turpentine and rectified naphtha, were also found to have inductive capacities greater than that of air.

Harris, by making use of discs of the different dielectrics of the same thickness, and coated on each side with tin-foil of less diameter than the dielectric, obtained the following results:

Air . . . . .	1.00	Bees-wax . . . . .	1.86
Resin . . . . .	1.77	Glass . . . . .	1.90
Pitch . . . . .	1.80	Shellac . . . . .	1.95

It appears then that solid dielectrics exhibit considerably greater inductive capacity than gases, but do not differ much in this respect among themselves. The results obtained with solid dielectrics are in fact just such as would follow if the metallic coatings were brought closer together, or, which comes to the same thing, if the charge were to penetrate to a certain extent within the substance of the dielectric. That such penetration takes place is well known; it is indeed the origin of the residual charge which is always found in a Leyden jar after it has been discharged (p. 387). Faraday has endeavoured to determine its amount in different dielectrics, so as to allow for it in calculating his results on specific inductive capacity. It is possible, however, that this disturbing cause has not been sufficiently allowed for, and that, if correctly estimated, it might be found fully adequate to account for the differences observed in the inductive powers of different insulators. Riees (*Reibungs-Electricität*, i. 356) attributes the entire effect to this cause. At all events, the experiments hitherto made are neither numerous enough, nor accurate enough, to establish a fact so important to the theory of electricity as that of specific inductive capacity.

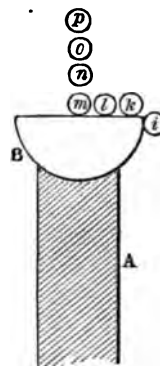
3. *Induction through dielectrics takes place, not always in straight lines, as commonly supposed, but very often in curved lines.*

When a charged body is placed in the midst of a dielectric medium, such as the air, with no conductors near, the particles of the dielectric become polarised in the manner already described, the inductive action radiating outwards in all directions in straight lines; but when conductors come in the way, the lines of inductive force change their direction, curving to a certain extent round the conductor, this curvature resulting, partly from the action of the conductors, partly from the mutual action of the polarised molecules of the dielectric, whereby a force is produced transverse to the lines of inductive force, and giving them a tendency to bulge outwards. This same transverse force is probably concerned in the magnetic action of the electric current.

For proof of this curvature of the lines of inductive action, Faraday relies, partly on the visible forms of the electric discharge in gases, as seen in the spark and more especially in the brush discharge, partly on certain experiments specially directed to the point, of which, as the mode of action is the same in all, it will be sufficient to cite the following. A cylinder of shellac A (*fig. 394*) set in a vertical position is excited negatively by friction; and upon it is placed a brass hemisphere B. An insulated carrier-ball is placed in contact with the hemisphere, and above it, in the several positions *i, k, l, m, n, o, p*, then uninsulated by touching it with the finger, insulated again, and then brought in contact with an electroscope or electrometer. In all cases, it is found to have received a *positive* charge. This charge is evidently a charge by induction, and Faraday regards it as a proof that the induction takes place from the surface of the excited lac through the air in curved lines, bending, indeed, round the surface of the brass hemisphere. The effects are exactly similar when a globe or a plate of brass is laid on the top of the excited shellac.

It is, however, not difficult to show that these and all similar phenomena are perfectly in accordance with the theory of action at a distance in straight lines. In fact, the apparatus represented in figure 394, is merely a modified form of the electrophorus, and the explanation already given (p. 385) of the action of that instrument may be applied, almost word for word, to the results obtained with Faraday's apparatus. The shellac stem being excited negatively, acts inductively on the brass hemisphere, rendering the lower surface of it positive, and the upper surface, together with any other conductor in contact with it, negative. When, however, the brass hemisphere is uninsulated, as by touching it with the finger, the negative electricity is driven into the ground, and the whole surface of the hemisphere, and of the carrier-ball in contact with it, as at *i, k, l*, or *m*, becomes positive; consequently, when the hemisphere is again uninsulated, and the carrier-ball made to touch an electrometer, it exhibits a positive charge. When the carrier-ball is held above the hemisphere, the latter is insulated, and the  $-E$  on its upper surface acts inductively on the carrier-ball at *n, o*, or *p*,

Fig. 394.





rendering it, while insulated, positive below and negative above, but when uninsulated, wholly positive, so that in this case also, the ball, when again insulated and carried to the electrometer, shows positive electricity.

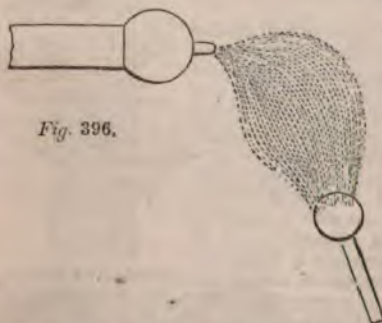
Faraday says, however, in allusion perhaps to such a mode of explanation, "To suppose that induction acts in some way through or across the metal, is negatived by the simplest considerations; but a fact in proof will be better. If, instead of the ball [or hemisphere] B, a small disc of metal be used, the carrier may be charged at or above the middle of its upper surface; but if the plate be enlarged to  $1\frac{1}{2}$  or 2 inches in diameter, then no charge will be given to the carrier when applied at the centre of its upper surface, though, when applied nearer to the edge, or even above the middle, a charge will be obtained; and this is true, though the plate may be a mere thin film of gold-leaf. Hence, it is clear that the induction is not *through* the metal, but through the surrounding air, or *dielectric*, and that in curved lines."

The non-charging of the carrier at the centre of the circular plate may, however, be explained in another way. When any conductor or chain of conductors whatever is placed under the influence of an electrified body, the two extremities of the conductor become oppositely electrified, and between the two there must be somewhere a neutral point or line. The exact position of this neutral point or line will depend upon a variety of circumstances, as on the form and size of the conductor, its distance from the charged body, and the strength of the original charge; but it must always be found somewhere, and there is no difficulty in supposing that, with the particular arrangement in question, it would be found at the centre of the plate. Indeed, with the hemisphere (*fig. 394*), the charge of the carrier-ball regularly diminished from the edges towards the middle, being  $112^\circ$  at *i*,  $108^\circ$  at *k*,  $65^\circ$  at *l*, and  $35^\circ$  at *m*; and with forms intermediate between the hemisphere and the flat disc, a regular gradation of charges at the middle point would doubtless be obtained.

But, as already observed, the action in this and all similar experiments, is merely that which takes place in the electrophorus, the condenser, the coated plate, and, indeed, in every conceivable arrangement in which a conductor is first placed under the influence of an electrified body, then uninsulated, and lastly insulated again. In all such cases, supposing the electrified body to be charged with  $+E$ , the  $-E$  of the conductor is drawn to its nearer extremity, and on uninsulating it, the  $+E$  is driven into the ground, so that, on again insulating the conductor, and removing it from the neighbourhood of the charged body, it appears *wholly negative*. The explanation of this effect on the commonly received theory of action at a distance, is clearer and more satisfactory than any explanation that has yet been suggested on the hypothesis of induction in curved lines.

The theory of induction in curved lines is further said to be supported by the fact that electric discharge, especially in the brush-form, frequently takes place in curves, as in *figs. 395, 396*, which represent the brush as formed between a charged con-

*Fig. 395.*



*Fig. 396.*

ductor and another on which it acts by induction. But in such cases, as well observed by De la Rive (*Traité*, i. 146), the curvature of the lines of discharge is not a primary, but a secondary effect, depending on the action of the conductors. The particles of air situated between the oppositely charged conductors become polarised, in the same manner as iron filings between two opposite magnetic poles, and arrange themselves in a similar manner. The curves of the electric discharge, as illustrated by the preceding figures, have, indeed, a strong general resemblance to the magnetic curves, as shown by iron filings. Now the form of the magnetic curves is determined by the joint action of the two magnetic poles, and depends upon the law of magnetic action with regard to distance: the curves are, in fact,

magnetic curves is determined by the joint action of the two magnetic poles, and depends upon the law of magnetic action with regard to distance: the curves are, in fact,



the graphic expression of the law of inverse squares (see Dela Rive, i. 592). Now it is not to be expected that the curves of the electric discharge between two conductors should exhibit the exact form of the magnetic curves; for they are disturbed by the influence of surrounding conductors, and by the continually shifting distribution of the charge on the surface of the conductors between which they are formed; nevertheless, the resemblance is sufficiently close to show that they are produced in a similar manner, and depend on the same law with regard to distance. Robison (*Mechanical Philosophy*, iv. 53) describes an experiment, in which a thin brass plate, coated with red sealing wax, was placed on two small insulated balls charged with opposite electricities, and a fine powder of black sealing wax was sprinkled on the plate from a considerable height; on tapping the plate gently with a glass rod, the fine particles of wax arranged themselves in curved lines, diverging from the point over each of the balls, just like iron-filings under the influence of a magnet.

The mutual action of conductors at a distance is then by no means inconsistent with the polarisation of the particles of the insulating medium; indeed, a number of non-conducting particles exposed to the action of two oppositely electrified bodies, or two centres of opposite electric force, *must* become polarised; but this is a very different thing from supposing that the charging of a conducting body by the influence of another cannot take place except through the intervention of those non-conducting particles. Whatever supposition we may make as to the manner in which a conductor becomes charged, whether (to use Faraday's expression) it polarises as a whole,—as if we suppose a quantity of electric fluid to be bodily transferred from one end of it to the other,—or whether the polarisation affects each individual particle, it is certain that conductors are more susceptible of electric influence than non-conductors (the terms are, of course, used relatively), taking a charge with facility, and returning with equal facility to their natural state when the disturbing force is removed. This being the case, we may expect that a conductor placed at a certain distance from a charged body will be electrified or polarised by its influence *before the intervening non-conducting particles*, just as if a number of very hard steel filings are strewn between a magnet and a bar of soft iron, the soft iron will be magnetised instantly, while the steel filings midway between the two will not become polarised, at least not to their full extent, for some considerable time. But further we may, while still retaining the hypothesis of action at a distance, suppose that a charged conductor is itself an aggregate of oppositely polarised particles. We know, from the phenomena of magnetism, that a heap of magnetised particles, with their similar poles all turned the same way, acts just as if one half of the mass possessed north, and the other half south polarity; thus a tube full of steel filings, magnetised by any of the ordinary methods, acts exactly like a magnet with a north pole at one end, a south at the other, and a medium line between them; in fact, in the middle of the mass, the opposite polarities neutralise each other, and show themselves only towards the ends. Just so must it be in a mass of particles, each of which has its two ends in opposite electrical states; the mass will act on external bodies, just as if one half of it were charged with  $+E$  and the other with  $-E$ .

This view of the state of a charged conductor may perhaps afford the true explanation of the well-known fact that the charge of a conducting body appears to be confined to its external surface. The ordinary theory attributes this superficial distribution to the mutual repulsion between the particles of the electric fluid, an explanation, which is perfectly satisfactory when once the hypothesis is admitted. Faraday, on the other hand, maintains that the charge of a conductor is confined to its surface, because it is only there that the particles of the conductor are in contact with those of the surrounding dielectric, by which alone their charged or polarised state can be retained. But why, on his own hypothesis, should not these superficial particles polarise those next to them, and these the next, and so on throughout the mass? It may be true that the particles of a charged conductor return to their natural state the instant they are removed from the influence of a disturbing force; but while the superficial particles are polarised, the interior particles must be subject to their influence. The fact that a proof-plane applied to the interior of a charged conductor receives no charge, proves nothing more than that all the forces there acting upon it balance each other, and their resultant is nothing; indeed it is just the same when the proof-plane is applied to the inner surface of a hollow metallic conductor, although the metal there is in contact with the air, just as much as on the outer surface.

In illustrating the action of the electric forces by the analogous phenomena of magnetism, we must be careful not to push the comparison too far. Up to a certain point electric induction, in its effects at least, is similar in every respect to magnetic induction. A charged body disturbs the electric state of another body in its neighbourhood, just as a magnet induces polarity in a neighbouring piece of iron, and in the one case as in the other, the disturbed body returns to its ordinary unpolarised state on the removal of the disturbing cause, provided, in the case of electricity, the charge or

disturbance does not go beyond a certain degree of intensity. But if that limit is passed, discharge takes place between the two bodies in the form of a spark or otherwise, and after that, neither of them returns to its former state when they are separated; the original charge then appears divided between the two, the one losing what the other gains, just as when a liquid is poured from one vessel to another. Now there is nothing in magnetism analogous to this: a steel magnet may induce the most intense polarity on a piece of soft iron in contact with it, so that the two can only be separated by the exertion of great force; but the separation once effected, every thing is as before; the soft iron loses all its magnetism, and the steel magnet returns to its original state of polarity.

In the representation which it affords of the phenomena of electric discharge—in other words, of the division of a charge between two bodies—the ordinary fluid theory has certainly the advantage of clearness and precision. Moreover, the transference of an electric fluid from one body to another is by no means incompatible with the polarization of contiguous molecules. A body may contain an excess of one or the other electric fluid, and at the same time that fluid may be accumulated on one side of each of its particles in larger quantity than on the other. Discharge may also be conceived to take place by transference of the electric fluids in opposite directions, from particle to particle, throughout the entire conducting chain. To explain this more fully, suppose a number of pieces of tin-foil to be pasted in a row on a plate of glass, and that one end of this row is presented to the conductor of an electrical machine, while the other is connected with the ground; a series of sparks will then be perceived at each interval between the pieces of tin-foil. Now suppose the number of these pieces to be increased, and the intervals between them diminished in width; the sparks will then be smaller, and the discharge more continuous; and if we imagine this diminution of the intervals to be continued indefinitely, they will at last become so small that the sparks will no longer be visible, but the discharge will take place with apparent continuity, as in a metallic rod; nevertheless, it will still be in reality a succession of discharges from one little piece of metal to the other. An electric current may, therefore, be regarded as a succession of charges and discharges, taking place between contiguous particles.

#### *Theory of a single Electric Fluid.*

Franklin attributed the phenomena of electricity to the action of a single electric fluid residing in all bodies, and capable of passing from one to another. The particles of this fluid are supposed to repel each other, and to be attracted by the particles of ponderable matter; and a body is in its natural or neutral electric state, when the quantity of electric fluid contained in it is such that the repulsion exerted by the whole of that fluid on a particle of electric fluid situated externally to the body, is equal to the attraction exerted on the same particle by the ponderable matter of the body. A body containing more than this natural quantity of electric fluid, is in the *positive* state, and exerts a repulsive action on the electric fluid of neighbouring bodies; and a body containing less than the natural quantity is in the *negative* state, and exerts an attractive action on the electric fluid in neighbouring bodies.

It is easy to see that this theory is capable of rendering an exact account of all the phenomena of induction and discharge. A body containing excess of electric fluid repels the fluid in a neighbouring conductor to the farther end, rendering that end positive, and the nearer end negative; and a body containing excess of ponderable matter attracts the fluid in a neighbouring conductor, rendering the nearer end of that conductor positive, and the farther end negative; and when the attraction between the electric fluid and the ponderable matter on the adjoining surfaces reaches a certain limit, a quantity of electric fluid passes from the positive to the negative surface, in the form of a spark, the redundant fluid of the positive body being then divided between the two. It is unnecessary to go into details; the explanation, in every case of charge and discharge, is the same as on the two-fluid theory, merely substituting the attraction between ponderable matter and electric fluid for that of the two electric fluids, one for the other.

The Franklinian theory has, however, been supposed to fail in accounting for the mutual repulsion of two negatively electrified bodies. When two bodies, pith-balls, for example, contain excess of electric fluid, the mutual repulsion of the particles of that fluid will cause it to be most concentrated at their farthest points, where, being prevented from going any farther, by the resistance of the air, it will cause the balls to fly asunder. But when the bodies contain less than their natural quantity of electric fluid, their mutual repulsion cannot be accounted for in a similar manner: hence Aepinus was induced to add to the Franklinian theory the assumption that *the particles of ponderable matter repel each other*. This assumption has usually been considered as opposed to the well-known fact of universal gravitation; but it is not

necessarily so: for, as pointed out by Roget, in his treatise on Electricity, in the "Library of Useful Knowledge," the tendency of any two bodies to move towards or away from one another, is the resultant of all the attractive and repulsive forces exerted between them; if, therefore, we suppose the sum of the repulsive forces (that is, of the particles of electric fluid for each other, and of the particles of ponderable matter for each other) to be slightly less, at the same distance, than the sum of the attractive forces (exerted between the particles of ponderable matter and electric fluid), there will remain a certain residual attractive force, which may constitute the force of gravitation.

On the other hand, we may observe that the assumption of a repulsive force between the particles of ponderable matter is not at all required to explain the phenomenon which gave rise to it. In fact, two negatively electrified bodies may be supposed to recede from each other, not because they actually repel each other, but because they attract one another less than either of them is attracted by the surrounding air,—just as a balloon rises in the air, not because it is actually repelled from the earth, but because it gravitates less than an equal bulk of air.

The Franklinian theory has been supposed to receive considerable support from the well-known appearance of the positive and negative brush (p. 389). The positive brush, with its divergent ramifications, does certainly suggest the idea of a fluid forcibly ejected through a narrow aperture, whereas the negative brush and glow have rather the appearance of streams of fluid converging towards an aperture; but the beautiful experiments of Faraday on the appearance of the electric discharge in different gases, show conclusively that the difference of character in the two brushes is much less absolute than was formerly supposed, and that it depends essentially on the nature of the medium. Gassiot, in one of his experiments on the electric discharge in vacuous tubes (Proc. Roy. Soc. ix. 605), speaks of "the appearance of a direction of a force emanating from the negative."

It would be difficult to single out any electrical phenomenon which affords a decisive argument in favour of the theory either of one or of two electric fluids. The two-fluid theory has, however, this advantage, that it represents the negative state of electric charge as the exact counterpart of the positive; whereas the one-fluid theory assumes a fundamental difference between the two, regarding one as arising from an excess, and the other from a deficiency, of electric fluid, without being able to say decidedly which is in excess and which in defect. The positive or vitreous state is indeed generally regarded as arising from excess of electric fluid; but, with the exception of certain appearances of the electric light just noticed, no difference has yet been pointed out between the phenomena of positively and negatively electrified bodies, capable of indicating in which of the two the excess is to be found.

Of late years, the study of the relations of electricity to heat, light, magnetism and mechanical force has led to the notion that its effects are due to peculiar arrangements and motions of the particles of ponderable matter, rather than to the movements of any peculiar fluid or fluids. And, however clear may be the view which the fluid theory affords of the phenomena of electric charge and discharge, it is not difficult to regard these phenomena, at least in their general features, from a different point of view. The opposite characters of the two electricities may be supposed to arise from two different kinds of motion among the particles of bodies, perhaps analogous to the vibrations of rays of light polarised in different planes; and the division of an electric charge between two bodies, may be compared to the division of velocity which takes place when a body in motion strikes another at rest or moving in a different direction.

In considering this question, however, it should not be forgotten that the phenomena of light, and certain disturbances in the motion of comets, point to the existence of an ethereal medium pervading space and filling up the intervals between the particles of ponderable bodies. Such a medium can scarcely be without influence on the electric state of a body; and, admitting its existence, it is by no means improbable that it may have a translatory as well as a vibratory motion, the former giving rise to the phenomena of electricity, the latter to those of light.

#### DEVELOPMENT OF ELECTRICITY BY MECHANICAL ACTION.

1. **By Friction.** The development of electricity by the friction of two solid bodies, one at least of which is a non-conductor, has already been considered (pp. 376, 377). We have now to notice the electric effects produced by the friction of pulverulent bodies, of conducting solid bodies, and of liquids.

Powders projected from a pair of bellows, become electrified by friction against the tube. Bennett made the curious observation, that powdered chalk, blown from a bellows against the cap of an electroscope, exhibited  $+E$  when the cap was



about 5 inches from the nozzle of the bellows, but  $-E$  when the distance was 6 inches. The powder is in fact positively electrified by friction against the tube of the bellows, negatively by friction against the cap of the electroscope, the one or the other of these effects predominating according to the distance. Pounded ice and very dry snow become electrified when blown from a bellows.

Powders become strongly electrified by passing through sieves. Pulverised earths and a large number of solid acids acquire negative electricity when sifted through organic tissues. Many powders become electrical when stirred. Dry oxalate of calcium stirred with a rod of glass or platinum becomes positively electrical in so high a degree that it is lifted out of the containing vessel on removing the rod (Faraday). Powders are also strongly electrified by rubbing against each other. When sealing wax and sulphur in powder are rubbed together, the wax becomes positive, the sulphur negative. When pounded resin (colophony) and red lead are rubbed together, the resin becomes negative, the red lead positive. A good way of exhibiting the opposite charges thus acquired by two powders, is to project them from a caoutchouc bottle having a glass tube inserted into its mouth and a piece of flannel tied over the tube, against two brass knobs (the knobs of two Leyden jars for example), oppositely electrified; the resin is then wholly deposited on the positive, the red lead on the negative knob. If the powders are projected against a resinous cake two points of which have been oppositely electrified, they collect round the points in very remarkable configurations, called *Leuchtenberg's figures*, the resin being deposited round the positive point in beautiful arborescent forms, the red lead round the negative point in round patches, or sometimes in concentric circles, altogether destitute of arborescent character. The difference is of the same kind as that between the positive and negative brush in air; it would be interesting to observe how the figures would be modified in atmospheres of different gases.

*Friction of Good Conductors.*—Metals and other good conductors do not exhibit any signs of electricity when rubbed together and then brought in contact with an electroscope, because the opposite electricities recombine more quickly than the surfaces can be separated. If, however, one of the metals, in the form of filings, is made to fall over the surface of the other, signs of electric charge become apparent, because the fine division diminishes the conducting power of the metal. Becquerel finds that when filings of any metal are projected against a plate of the same metal, the filings become negative, and the plate positive, the effect being stronger as the metallic powder is finer and more rapidly projected. When the plate and the filings are of different metals, the effect is complicated by the electric charge resulting either from simple contact of the two, or from chemical action exerted on one of them by the moisture in the air (p. 414), so that the effect due to friction cannot be exactly ascertained. Copper filings become negative when projected against plates of zinc, lead, tin, iron, bismuth, and antimony; zinc filings positive with plates of platinum, gold, silver, copper, and tin,—negative, with plates of zinc, bismuth, antimony, and iron. Pulverised metallic oxides and sulphides are positive with respect to the corresponding metals.

To exhibit the electricity developed by rubbing together solid pieces of good conductors, it is necessary to make use of the galvanometer. Solder a narrow strip of copper plate to one end of a galvanometer wire, and a similar strip of iron plate to the other end, and enclose the junctions, together with a portion of the plates, in corks, to serve as handles, so that no heat may be communicated from the hand to the metal. If the two plates are then simply brought in contact, no electric effect will be apparent; but on rubbing one plate lightly over the other, taking care to separate the rubbed parts as quickly as possible, but still maintaining the contact, the needle of the galvanometer will be deflected, its direction indicating the passage of a current of positive electricity from the iron through the wire to the copper, and therefore showing that the iron has been rendered positive by the friction, and the copper negative. Of the bodies in the following table, each one, when thus treated, becomes negative with all those which follow, positive with all those which precede it: *Bismuth, palladium, platinum, lead, tin, nickel, cobalt, copper, gold, silver, iridium, zinc, iron, cadmium, arsenic, antimony, anthracite, peroxide of manganese*. This is the same as the thermo-electric series (p. 412); nevertheless, the effects do not appear to be due to heat; for, if two cylinders, about 4 inches long, one of copper, the other of iron, are attached to the ends of the galvanometer wire, and rubbed together in such a manner that the same points of the one may traverse the entire length of the other, whereby these points are heated much more strongly than the surface, the same current is obtained, both in direction and in intensity, whether the iron be rubbed in this way over the copper, or the copper over the iron. The degree of heat evolved in either of the metals is, therefore, without influence on the result.

*Friction of Liquids.*—It was formerly supposed that electricity is not developed by

the friction of liquids against solid bodies. Subsequently, however, it was found that liquids, in the form of very small globules, either alone or mixed with air, yield a considerable quantity of electricity by friction against solids; alcohol, ether, and liquid resins, projected in this manner against rough glass, render it strongly positive. Mercury may be rendered highly electric by friction. When a small quantity of mercury, contained in a foot-glass, is connected by an iron wire with a gold-leaf electroscope, and a solid body, such as a glass rod, partially immersed in it, no signs of electric excitement are manifested during the immersion; but on gradually withdrawing the solid body, the leaves of the electroscope diverge, the excitement increasing as the solid body is withdrawn, and reaching its maximum at the moment when it leaves the mercury. With organic substances, such as paper, linen, wool, woollen cloth, silk, sarcenet, feathers, and felt, the mercury takes a positive charge; with feathers and felt, when very dry, it sometimes gives sparks. Most mineral substances (*e.g.* rock-crystal, sulphur, and glass), render the mercury negative; amber and sealing-wax give it a strong positive charge.

Very large quantities of electricity are developed by the friction of water, in the form of minute globules, against solid bodies. Steam escaping from boilers often exhibits positive, and the boiler, if insulated, negative electricity. If one hand, or a plate of metal, or a bundle of wires with numerous points, be held in the stream of vapour, and the other brought near the boiler, a spark may be obtained from the boiler. This effect, accidentally discovered by a workman in Sir William Armstrong's factory at Sighill, near Newcastle, was carefully investigated by the latter (*Phil. Mag.* [3] xxii. 1), who found that the intensity of the electric charge increased with the pressure of the steam, and that the steam was in most cases positive, the boiler negative. Armstrong attributed the electric excitement to the expansion of the vapour; but Faraday, by a very careful analysis of the phenomenon (*Experimental Researches*, ser. 18), has shown that electricity is never excited by the passage of pure steam, and is manifested only when water is likewise present. Hence he concludes that the effect is altogether due to the friction of the globules of water against the sides of the opening, or against the substances opposed to its passage, as the water is rapidly moved onwards by the current of steam. Accordingly, it is found to be increased in quantity by increasing the pressure and impelling force of the steam. The immediate effect of this friction is, in all cases, to render the steam positive, and the solids, whatever they might be, negative. A wire placed in the current of steam at some distance from the orifice, exhibits the positive electricity acquired by the steam, of which it is then merely the recipient and conductor. The results may be greatly modified by the shape, nature, and temperature of the passages through which the steam is forced. The electric charge is greatly increased by causing the jet of steam to issue from a tube of hard wood. With an ivory jet, on the contrary, very little electricity is produced. Heat, by preventing the condensation of the steam into water, likewise prevents the evolution of electricity, which, however, speedily appears on cooling the passages, so as to restore the water which is necessary for the production of that effect. The phenomenon of the evolution of electricity in these circumstances is dependent also on the *quality* of the fluid in motion, more especially in relation to its conducting power. Water will not excite electricity, unless it be pure: the addition of any soluble salt or acid, even in minute quantity, is sufficient to destroy this property. The addition of oil of turpentine, on the contrary, occasions the development of electricity of the opposite kind to that which is excited by water; each particle of the water then becomes covered with a thin film of oil, so that the friction takes place only between that external film and the solids along whose surface the globules of liquid are carried. A similar but more permanent effect is produced by the presence of olive-oil, which is not, like oil of turpentine, subject to rapid dissipation.

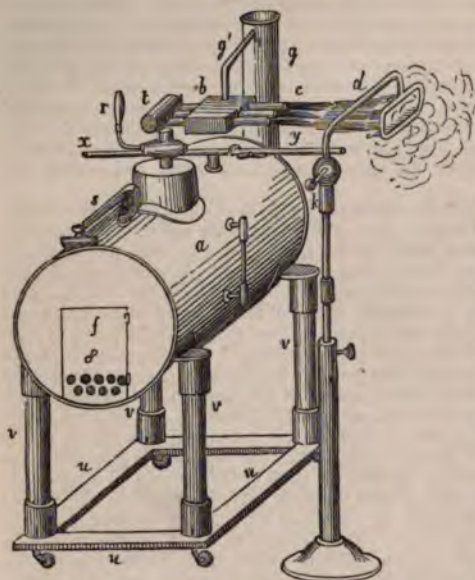
Compressed air, when pure and dry, does not exhibit any sign of electricity when issuing from an orifice; but if damp, it acquires positive electricity, and renders the vessel negative, the effect being due to the particles of water condensed by the cold arising from the sudden expansion of the air. The escaping air likewise becomes electric if it is impregnated with fine dust or powder of any kind. Thus, when air, containing finely divided sulphur, issues from a mouth-piece of metal, wood, or sulphur, the air acquires  $+E$ , the vessel  $-E$ ; powdered resin renders the vessel negative if the mouth-piece is of metal, positive, if it is of wood; starch-powder renders wood negative; very finely divided silica imparts  $+E$  to metals or to wood. The discharge of a dusty air-gun in the dark is attended with a flash of light, which is probably due to electricity developed in a similar manner.

The general conclusion to be drawn from the experiments above described, is that electricity is excited by friction between two solid bodies, or between a solid and a liquid; but that the friction of gases against solids does not produce any development of electricity.



The electric excitement resulting from the friction of water is applied to the construction of an electrical machine of great power, called the HYDRO-ELECTRIC machine. It consists essentially of a cylindrical boiler *a* (fig. 397), a set of escape-tubes *c*, partly

Fig. 397.



enclosed in a condenser *b*, and a conductor *d*. The boiler, which is usually about 15 inches in diameter and 30 inches long, is heated by an interior fire-place fed with charcoal; *f* is the fire-door, *g* the chimney. The boiler is supported on four strong glass legs *v*, fixed to a frame which stands on castors *u*; *s* is the safety-valve; *r* a cock for letting off the steam, and setting the machine in action, the steam first passing into the tube *t*, thence into the three small horizontal tubes passing through the condenser *b*, and issuing by the mouth-pieces *c*. The condenser *b* contains cold water, not, however, reaching to the level of the horizontal tubes, but supplied to them by cotton wicks hung over them, and dipping into the water; the wicks thus become moistened by capillarity, and cool the tubes just sufficiently to condense a portion of the steam. The steam which

forms within the condenser escapes into the chimney by the tube *g*.

The construction of the mouth-pieces is of great importance; in fact, the power of the machine mainly depends upon them. The escape-tubes near their extremities are widened in the form of a cone (fig. 398), and within this cone is introduced a piece of

Fig. 398.



of hard wood *p*, having the form of a truncated cone, the smaller base of which is joined to the piece of metal *m*. The current of vapour striking against this piece of metal is divided, and forced to enter the slit; where it is again divided and passes into the tube in the axis of the wooden cone; the screw ring *n* serves merely to keep the different parts of the mouth-piece together.

As the steam passes through the condenser, part of it is reduced to minute drops of water, which pass on with the steam, and it is by the friction of these drops of water against the wood that the electricity is developed; in fact, the drops of water correspond to the rubber of an ordinary electrical machine, the wooden mouth-piece to the plate or cylinder, and the steam is merely the motive power serving to produce rapid friction.

The steam, as it issues from the tubes, impinges against a number of metallic points at the top of the conductor *d*, and charges the conductor with  $+E$ ; this conductor is insulated, and sparks are taken from the ball *K*.

The tube *xy* serves to introduce different pulverulent substances into the course of the steam in order to study their influence on the nature of the electricity developed.

The hydro-electric machine yields large quantities of electricity, and of very high intensity. A gigantic machine of this kind, exhibited a few years ago at the Polytechnic Institution, having a boiler  $3\frac{1}{2}$  feet in diameter and  $6\frac{1}{2}$  feet long, charged a battery containing 36 square feet of coated surface in half a minute, and gave sparks 22 inches long, which instantly set fire to tow filled with pounded resin, and to a heap of wood-shavings,—effects which, with the ordinary electrical apparatus, can only be produced by the discharge of a large jar.

The hydro-electric machine is not, however, very well adapted for general use. It cannot be used in an ordinary apartment, as, besides the inconvenience of the fire, it



is necessary to provide some means of carrying off the steam, otherwise the atmosphere soon becomes quite unfit for electrical experiments. Moreover, to get up the steam to the required pressure, the fire must be kept up for several hours, and to keep the machine in a proper state of efficiency, the interior must be cleaned from time to time by heating a solution of potash in the boiler, blowing it through the tubes, and then washing out with pure water.

**2. By Pressure.** Friction is not the only kind of mechanical action by which electricity may be developed; indeed, every molecular movement of a solid body, however produced, appears to be attended with a disturbance of the electric equilibrium.

Solid bodies become oppositely electrified when merely pressed together and afterwards separated.

When two parallel faces, natural or artificial, of a mineral are pressed between the fingers, the mineral frequently becomes electrical on these surfaces, generally showing positive electricity. Calcspar retains the electricity thus developed from three to eleven days, topaz and fluor-spar several hours, mica one or two hours, and rock-crystal for a shorter time. Talc must be insulated in order to render it electrical; heavy spar and gypsum are not sensibly electrified (Hauy).—According to Becquerel, not a trace of electricity is perceptible while bodies are being pressed together; it is not till they are separated that the one appears positively, the other negatively electrified. A slice of cork becomes positively electrified when pressed against a slice or plate of caoutchouc, orange-peel, retinasphalt, coal, amber, zinc, copper, silver, kyanite, or heated double refracting spar, these substances at the same time becoming negative. On the contrary, the slice of cork becomes negative with all dry animal substances, with heavy spar, gypsum (which must be freed by drying from hygroscopic water), fluor spar, and double refracting spar, not heated,—those substances at the same time becoming positive. Two good conductors pressed together exhibit, when separated, no other electricity than that developed by mere contact. Two similar bodies do not become electrical by pressure, unless one of them is at a higher temperature than the other; and then the hotter body always becomes negative, the colder positive. The strength of the electricity thus developed depends upon the nature of the bodies, the state of their surfaces, the intensity of pressure, and the rapidity of separation. Cork produces more electricity with calcspar, when the pressure is exerted on one of the faces parallel to the cleavage-planes, than with heavy spar; with the latter more than with polished rock-crystal, and with this more than with gypsum, or with the polished surface of calcspar; and when pressure, temperature, dryness, and polish of the cleft surfaces are equal — three times as much with calcspar as with gypsum. The intensity of the electricity varies directly as the pressure; so that when the latter is doubled, the former is doubled also. Lastly, if the two bodies which have been pressed together are slowly separated, the two electricities have time to reunite, and a much smaller quantity remains in the free state after the separation. Bodies rendered electrical by pressure retain the electricity for a longer time, in proportion as their insulating or non-conducting power is greater.

**3. By Cleavage and Separation of Surfaces.** When two laminae of a crystal of mica are suddenly torn asunder, there is not only an appearance of light produced, but one lamina becomes positively, the other negatively electrified; if again pressed together and subsequently separated, they again appear electrified. Also, on the cleavage of calcspar, fluor-spar, heavy spar, topaz, talc, and dry warmed gypsum, and on tearing a playing-card into its two sheets, the separated laminae appear oppositely electrified. In topaz, whose cleavage takes place parallel to the terminal faces of the prism, the cleft surface belonging to one end of the prism exhibits sometimes one kind of electricity, sometimes the other. When melted shellac is poured upon glass and pulled off after cooling, both become electrified. Non-crystalline bodies, such as sealing-wax or glass, exhibit no electricity when broken.

Two sheets of paper stick fast together when rubbed with india-rubber, and, on being pulled asunder, appear strongly charged with opposite electricities, often sufficiently to give sparks.

The electric effects obtained in the solidification of fused substances depend, like the preceding, on a disaggregation, or forcible separation of particles. When melted sulphur is poured into a short glass vessel of conical shape, and a glass rod is inserted into the sulphur before it solidifies, no electricity is apparent so long as the sulphur remains in the glass; but on lifting out the solid cone by the glass handle, the sulphur exhibits  $+E$ , the inner surface of the vessel  $-E$ . Similar effects are exhibited by chocolate and glacial phosphoric acid when melted and left to solidify in glass vessels. The development of electricity in these cases depends on the separation of the two surfaces by the contraction of the melted mass; substances which expand on

cooling, like fusible metal, exhibit no electricity when left to solidify in glass vessels. Hence Gay-Lussac concluded, that the change of state from the liquid to the solid is not a direct source of electric excitement, but merely serves in some cases to produce a molecular disaggregation, which is the true source of the electricity. If sulphate of copper and potassium be brought into a state of red-hot fusion in a platinum crucible, connected by a ring of wire on which it rests with a Bohnenberger's electroscope (p. 428), and then left to cool, no electricity will be apparent during the crystallisation; but as soon as the crystalline mass begins to contract with an audible decrepitation, and falls to pieces gradually and spontaneously, the formation of each new fissure is accompanied by a development of electricity, and the effect goes on till the whole crumbles to dust. (Böttger, Pogg. Ann. l. 43.)

**4. By Vibration.** When a metal rod having one of its ends coated with resin, is made to slide through an insulated metallic ring, so that vibrations may be produced in the metal, and communicated to the resinous coating, the rod and the coating both become electrical; the kind of electricity developed in each of them depending on the direction in which the rod is moved. When the rod slides through the ring with the covered end in advance, the uncoated portion of the rod, and therefore also the inner surface of the resinous coating, becomes negative: the outer surface of the coating at the same time becoming positive, as may be shown by hanging a small metal ring over it, and connecting this ring by a thin wire with a delicate gold-leaf electroscope. On reversing the movements, the electric charges are likewise reversed. If both ends of the rod are coated, and connected in like manner with electroscopes, they exhibit opposite electricities at each movement of the rod.

Different metals exhibit this effect in various degrees; brass and silver much more strongly than iron or steel. The effect is due to the longitudinal vibration produced in the rod, which sets the particles of the resinous coating also in vibratory motion, and seems to cause them to arrange themselves in a polar chain, so that the two surfaces of the layer exhibit opposite polarities. That it is not due to mere friction is proved by the fact, that the direction of the electric polarity remains the same as above when the ends of the rod are coated with sulphur, but is reversed when they are covered with pieces of glass tube; it is likewise unaltered when the inner surface of the ring is coated with various substances. When rods composed entirely of resin, sulphur, or glass are used, the effects are the same as when the ends of a metal rod are coated with these substances; glass, however, becomes much more strongly excited than resin or sulphur, because it is more elastic and vibrates better. It is remarkable that these effects are produced quite as strongly in a vacuum as in air. (Volpicelli, Compt. rend. xxxviii., 15 Mai, 1854).

When the ends of a galvanometer wire are connected by a wire composed of brass and iron soldered together, and this compound wire is stretched and made to vibrate so as to give out a musical sound, the needle is immediately deflected, indicating the production of an electric current. A compound bar of antimony and bismuth soldered together, end to end, 25 centimetres long, 10 mm. wide and 7 mm. thick, exhibits this effect very strongly when connected with a galvanometer, and struck with a piece of iron. A similar effect may be obtained with a bar of a single metal, iron, for example, one portion of which is hard and crystalline, the other soft and fibrous, (Sullivan, *Archives d'Electricité*, x. 480). Ermann (*ibid.* v. 477) has also shown that when different metals are combined together, as for thermo-electric couples (p. 412) and rubbed slightly at the point of contact, currents are produced in the same direction as if heat were applied. The effect is not, however, due merely to heat developed by the friction, but is a direct result of the vibration or molecular disturbance thence resulting; for the current shows itself the instant that the friction commences, and ceases when the friction is discontinued, however long it may have been kept up.

When a long unannealed copper wire supported at intervals on props, is connected with a galvanometer, so as to form a closed circuit, and one part of it raised or lowered, and then released so as to throw the wire into vibration, an electric current is sometimes produced. If the needle does not move, it is probable that equal and opposite currents are produced in different parts of the wire; in that case, if one part of the wire be hardened by hammering or twisting, and the movement then repeated, a current will be produced. These currents are not due to the inductive action of the earth's magnetism; for they are produced in the same way whether the wire be placed parallel to the magnetic meridian, or inclined to it at any angle whatever. (Peltier, *Archives d'Electr.* i. 145).

It appears then that every molecular disturbance taking place in a solid body is attended with a development of electricity. Whether the electric polarity thus produced actually consists in a peculiar arrangement of the molecules of the body, or in particular movements imparted to them, or arises from a new arrangement of the

electric fluid or fluids associated with them, is a question which cannot at present be answered. But the whole of the phenomena just described appear to indicate that the electric polarity, whatever it may be, affects each separate particle of the body. We may suppose indeed that the separate particles of bodies are always in a polarised condition; but that when a body is in its ordinary state, the poles of the several particles are disposed without any regular order, so that their resultant action on any external particle is nothing, and that electric excitement consists in turning all the similar poles in one direction,—just as a glass tube filled with steel-filings acts like a bar-magnet when the filings are all regularly magnetised, but loses its polarity when the regularity of the arrangement is disturbed by shaking. The opposite electrification exhibited by two surfaces of a crystalline substance, like mica, when broken, may be compared to the effect of breaking a bar-magnet in two, and seems to show that the opposite polarities of the particles of the crystal neutralise each other when in contact, and manifest themselves when separated. The comparison must not, however, be carried too far: for if a crystal were made up of polarised particles symmetrically arranged, it would constantly exhibit opposite polarities at its two ends. The effect of motion, in allowing the particles of a body to assume the symmetric arrangement essential to electric polarity, is strikingly shown by the experiments of Volpicelli and by those of Sullivan and Ermann; the latter also indicate a close connection between the effect of mechanical disturbance and that of heat, which we now proceed to consider.

#### DEVELOPMENT OF ELECTRICITY BY HEAT.

1. *In Crystals:—Pyro-electricity.*—Many crystals, while their temperature is rising or falling, exhibit contrary electricities at their opposite ends, those extremities, or poles, which are positive while the crystal is being heated, becoming negative while it cools. The effect is altogether dependent on *change of temperature*, no crystal exhibiting any electric polarity while its temperature remains constant.

That pole of a crystal at which the algebraic sign of the change of temperature is the same as that of the electricity developed (*e. g.* which exhibits  $+E$  while the temperature is rising) is called the analogous pole; the other, the antilogous pole.

The electric polarity of crystals appears to be essentially related to hemihedry, and in many instances to the non-superposable hemihedry exhibited by substances which possess the power of circular polarisation (see CRYSTALLOGRAPHY, p. 157). It was first observed in the tourmalin, which has long been known to possess the power of attracting light bodies when heated. This mineral usually crystallises in nine-sided prisms of the hexagonal system (*fig.* 399), which may be conceived to be formed from the triangular prism  $\frac{8P2}{2}$  (CRYSTALLOGRAPHY, p. 143) having each of its edges bevelled

by two small prismatic faces, and acuminated at both ends by three rhombohedral faces (denoted by P in the figure), which at one end, *a*, are set upon the faces of the triangular prism, and at the other end, *b*, on its edges. The end *a* is the analogous pole, becoming positive when the crystal is heated, negative as it cools.

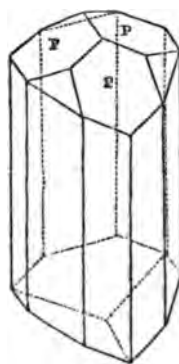
The manifestation of electric polarity in the tourmalin is confined within certain limits of temperature, mostly between  $10^{\circ}$  and  $150^{\circ}$  C.; these limits vary, however, according to the length of the crystal.

A heated crystal of tourmalin suspended by its centre may be attracted and repelled by electrified bodies, just as a magnetic needle is attracted and repelled by other magnets; it further resembles a magnet in this respect, that on breaking it across, while still in the electrically polarised state, each of the fragments is found to have a positive and a negative pole, showing that the electric polarisation affects each individual particle, and that in the excited crystal all the particles have their poles symmetrically disposed.

In most crystals, the electric polarity is much less powerful than in the tourmalin, and in some cases can only be detected by the use of a delicate electroscope; but the general laws affecting it are the same in all.

In boracite, which crystallises in the form  $\infty O \infty \cdot \frac{O}{2}$  (*fig.* 400), the four cubic summits which are truncated by shining tetrahedral faces, are antilogous poles; the other four, which are either not truncated at all, as in the figure, or truncated by dull tetrahedral faces, are analogous poles. Silicate of zinc, or siliceous calamine, which

*Fig.* 399.







The word "and" in this table is placed between two metals of equal thermo-electric power. The dash separates the thermo-positive from the thermo-negative metals (see below). The discrepancies in the statements of different experimenters induce the supposition that the direction of the current is affected by impurities in the metals, and varies with the difference of temperature. That the latter may really be the case, will appear from the following:

When iron is moderately heated in contact with copper, silver, gold, brass, or zinc, positive electricity proceeds from the iron through the galvanometer to the copper, &c., but when the heat is stronger, from the copper, &c., to the iron (Cumming). The reversal of the direction of the current takes place at a dull red heat, when copper and iron are the metals employed (Becquerel). Zinc and gold produce at  $70^{\circ}$  C. a feeble current which passes from the zinc through the galvanometer to the gold; at  $150^{\circ}$ , this current ceases; at  $180^{\circ}$ , an opposite current sets in, and becomes very strong at  $275^{\circ}$ . On the contrary, with zinc and silver at a low temperature, positive electricity passes from the silver through the galvanometer to the zinc. This current attains its greatest strength at  $120^{\circ}$  C., diminishes at a higher temperature, ceases at  $225^{\circ}$ , and is reversed at still higher temperatures. (Becquerel.)

The farther two metals are separated in the thermo-electric series, and the higher the temperature at the point of junction, the stronger is the current; but it is always small in quantity and of very feeble tension.

By combining a number of thermo-electric pairs into a *thermo-electric battery*, *chain*, or *pile*, a powerful thermo-electric current may be obtained: e. g. a number of bars of bismuth and antimony, or of platinum and iron, alternately soldered together

Fig. 402.

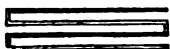
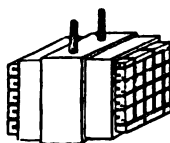


Fig. 403.



(Figs. 402, 403), and heat applied to the first, third, fifth, &c., points of junction, whilst the second, fourth, &c., are kept cold. In this manner the thermo-electric current produces, not only deflection of the needle, but likewise chemical decomposition of liquids (Bottó, Pogg. Ann. xxviii. 238), and heating effects, so that even when one of the conducting wires of the battery is cooled by immersion in ice, the point of junction of that wire situated without the ice becomes sensibly warmed (Watkins, Phil. Mag. [3] xiv. 82; also Pogg. Ann. xvi. 497). Melloni's *Thermo-multiplier*, or *Thermoscope*, is a pile formed in this manner of bars of bismuth and antimony, and connected with a galvanometer. The rays of heat fall on the first, third, fifth, &c., points of junction, whilst the second, fourth, &c., are kept cool. The smallest difference of temperature between the two sets of junctions suffices to produce deviation of the needle.

*b. With one Metal.*—A metallic wire connected with the two ends of a galvanometer gives no electric current when heated in the middle: but when each end of the galvanometer is connected with a wire, and the end of one of the wires is heated and then quickly pressed on the cold end of the other, an electric current becomes manifest by the deflection of the needle of the galvanometer. The direction and strength of this current vary with the nature of the metal employed. In the so-called *thermo-positive metals*, bismuth, platinum, gold, silver, copper, tin, lead, &c., the positive electricity goes from the cold piece of metal through the galvanometer to the hot piece; in the *thermo-negative metals*, zinc, iron, antimony, &c., from the hot to the cold end. The more one end is heated, the stronger is the current. According to Yelin, bismuth produces the strongest current with a given degree of heating; then follows antimony, then zinc, silver, platinum, copper, brass, gold, tin, and lastly lead; but, according to Nobili, this order is correct for certain temperatures only.

A simple platinum wire connected with a galvanometer also produces a current when heated, if it be tied in a knot at one point and heated near the knot; because the more rapid cooling through the knot causes unequal distribution of heat on the two sides; the positive electricity proceeds from the knot through the galvanometer to the heated part. Two copper wires do not produce so strong a current when clean as they do when covered with oxide or with a thin film of silver or gold, because the covering hinders the communication of heat to the cold end, and consequently interferes with its uniform distribution (Becquerel). Mercury is not thermo-electric, according to Matteucci and De la Rive; very slightly, according to Peltier.



## DEVELOPMENT OF ELECTRICITY BY CHEMICAL ACTION—GALVANIC OR VOLTAIC ELECTRICITY.

Chemical action is always accompanied by a disturbance of the equilibrium between the molecules of a body, and may therefore be expected to give rise to electric excitement. It is, in fact, the most powerful of all causes of electric action, though it does not appear to be so in all cases, because the opposite electricities recombine, for the most part, as fast as they are separated, unless particular arrangements are made to prevent such recombination. In fact, in this, as in other modes of development, the quantity of electricity which becomes apparent, generally forms but a small portion of that which is actually set free.

The development of electricity by chemical action will be considered under the following heads:

1. Between a liquid and a solid.
2. Between two liquids.
3. Between a gas and a liquid or solid.
4. By combustion.

Of these the first is the most important, as it is that which forms the basis of the ordinary voltaic battery.

1. *Development of Electricity by the Chemical action of Liquids on Solids.*  
VOLTAIC BATTERY.

When a metallic capsule containing a conducting liquid, viz. water or any aqueous solution, is placed on the cap of a delicate condensing electroscope (p. 386), and a piece of another metal held between the fingers is immersed in the liquid, without touching the capsule, the leaves of the electroscope diverge with  $+E$  or  $-E$  according to the nature of the metals and of the liquid interposed between them. If the capsule is of platinum, the electroscope shows that it has taken a charge of  $+E$ , whatever may be the nature of the liquid and of the metal dipped into it. A copper capsule on the other hand becomes positive or negative, according as the metal dipped into the liquid is more or less attacked by that liquid than the copper capsule itself. The result in all cases resolves itself into this, that when a metal is acted upon by a liquid, the metal becomes charged with  $-E$ , the liquid with  $+E$ . Thus, when zinc is plunged into water contained in a platinum capsule, the zinc takes  $-E$ , which passes into the ground, and the  $+E$  taken up by the water is transferred to the capsule and thence to the upper plate of the condenser; consequently the gold leaves connected with the lower plate exhibit a negative charge. Similarly with zinc, water, and copper. If, on the other hand, a piece of platinum or gold is plunged into nitric acid contained in a copper capsule, the copper becomes negative and the leaves of the electroscope diverge with  $+E$ . If both metals are attacked by the liquid, the charge of the condenser is that which results from the difference of the two actions.

The effects just described are exactly the same whether the metallic capsule and the plate of the condenser on which it rests are formed of the same or of different metals; they cannot therefore be due, as is sometimes supposed, to electricity developed by the contact of dissimilar metals; in fact, as already observed, the kind of electricity taken up by the capsule depends altogether on the reaction which takes place between the two metals and the liquid. Moreover, it has been distinctly shown by De la Rive and others, that contact of dissimilar metals is not accompanied by development of electricity, unless one of the metals is at the same time chemically acted upon by the moisture of the air, or by some other liquid. See De la Rive (*Traité*, ii. 773-787), and Wiedemann (*Die Lehre vom Galvanismus und Electromagnetismus*, i. 17).

The signs of electric tension exhibited by the arrangements above described are feeble, even when the chemical action is highly energetic, and require a very delicate electroscope to render them visible. The cause of this apparent anomaly is that, the metal and the liquid which act upon it being both conductors and remaining in contact, the greater part of the opposite electricities recombine as fast as they are separated. Accordingly, the electric tension may be greatly increased by causing the liquid to evaporate at the instant that the chemical action takes place. Thus, when a capsule of any oxidisable metal, copper, zinc, or iron for example, is strongly heated, then laid on the plate of the electroscope, and a few drops of water either pure or slightly acidulated poured into it, the liquid attacks the hot metal and vaporises at the same time; consequently the  $+E$  is carried off by the vapour and cannot reunite with the  $-E$ , which therefore passes into the electroscope, and produces a strong divergence of the gold-leaves, even without the aid of a condenser. If the quantity of water introduced is too great to be completely vaporised, scarcely any divergence is produced,



because the two electricities can then reunite, the  $+E$  not being carried off by the vapour.

The development of electricity in this manner was observed by Volta and De Sausure, who ascribed it, not to chemical action, but to the vaporisation of the liquid. But it is easy to show that this view is not correct: for if a clean platinum capsule strongly heated be laid on the cap of the electroscope, and a few drops of water or any other liquid which neither acts upon the platinum nor is decomposed by the heat, be thrown into it, no signs of electricity are manifested. It is necessary, however, to use a shallow capsule with the lip not turning inwards; otherwise electricity may be developed by the friction of little globules of water carried away by the steam against its sides (p. 407). If the water contains any salt in solution, electricity will be developed by the separation of the water from the salt.

The development of electricity by the oxidation of a metal may likewise be shown without the aid of heat. If a small piece of potassium be spread on the bottom of a platinum capsule connected with a condenser, a drop of water let fall on the potassium, and the plate of the condenser lifted up as soon as the hydrogen-flame produced by the decomposition of the water has ceased, the electroscope gives signs of electricity, showing that the capsule has been charged with  $-E$ , the  $+E$  having been carried away by the hydrogen and aqueous vapour evolved.

Fig. 404.



The electricity developed by chemical action may be made to show itself in the dynamic, much more easily than in the static form. When a plate of zinc and a plate of platinum are immersed in dilute sulphuric acid and connected outside the liquid by a wire (Fig. 404), a current of electricity is immediately set up, continuing as long as the conducting circuit is complete and the action of the acid on the zinc goes on. This may be shown by placing a magnetic needle near any part of the connecting wire; the needle is then deflected, tending to place itself at right angles to the wire; and the position of its poles shows that the current of  $+E$  passes from the zinc through the liquid to the platinum and thence through the wire to the zinc, as indicated by the arrow in the figure, this direction being in accordance with the charging of the condenser by an arrangement of zinc, acid, and platinum as before described (p. 414).

The greater facility with which the electricity thus developed shows itself in the form of a current is easily explained. The  $+E$  taken up by the liquid and thence transferred to the platinum, can unite with the  $-E$  of the zinc in two ways, either through the liquid, or through the connecting wire, and as the latter possesses greater conducting power than the liquid, the greater part of the opposite electricities recombine along the wire; whereas if the one or both of the plates are insulated, as when the arrangement is made to charge an electroscope, they recombine through the liquid, and only very small quantities show themselves on the plates in the state of tension.

The system of two dissimilar metals immersed in a liquid which acts on one of them is called a GALVANIC or VOLTAIC COUPLE. Its peculiar powers were first observed by Galvani, who found that the hind legs of a frog touched in different parts by a copper and an iron wire in contact with each other, were thrown into convulsions. Galvani did not however notice the necessity of having two metals to produce the effect; this most important point was discovered by Volta, who attributed the effect to electricity developed by the contact of the dissimilar metals, and by theoretical considerations founded thereon, was led to the invention of the pile or battery which bears his name. We now know that the electricity in Galvani's experiment was developed, not by the contact of the metals, but by the chemical action of the moisture on the frog's leg on one of the metals, viz. the iron. The necessity of having two metals in this or any similar arrangement is obvious; for if two plates of the same metal were immersed in a liquid, and connected by a wire outside, they would tend to produce equal and opposite currents, and no electricity would be apparent.

Of the two metals in a voltaic couple, that which is most attacked by the liquid is called the positive, the other the negative metal. It must be remembered, however, that it is the inactive metal from which the current of  $+E$  passes into the conducting wire, and that this metal, though called negative, really corresponds, in its relations to the external conducting channel, with the positive conductor of the electrical machine, or the positive surface of a coated plate. The term positive, as applied to one of the metals of a couple, must be understood as denoting that which determines the direction of the current. The following experiments will show that

the direction of the current is really determined in this manner, and therefore that it owes its origin to chemical action:

When two plates, one of gold and the other of platinum, are connected with a delicate galvanometer and immersed in pure nitric acid, no current is produced; but on adding a drop of hydrochloric acid, a strong current is excited, proceeding from the gold through the liquid towards the platinum, because the gold is attacked by the nitro-hydrochloric acid, while the platinum is much less acted on, if at all (De la Rive). When two gold wires connected with the ends of a galvanometer coil are immersed in pure nitric acid, no current is produced; but on adding a small quantity of hydrochloric acid to the part of the liquid near one of the wires, a current is set up from that wire through the liquid to the other (Becquerel). In like manner a couple formed of platinum and palladium, which is inactive in dilute sulphuric acid, becomes active on adding a few drops of nitric acid, which produces an action on the palladium and renders it positive; similarly, a couple of rhodium and platinum, inactive in nitric acid, becomes active on addition of hydrochloric acid, the platinum being then attacked. (De la Rive.)

Moreover, the direction of the current in a voltaic couple is in many cases reversed on changing the liquid in which the metals are immersed. Let a copper plate or wire be attached to one end of the coil of a galvanometer, and an iron plate or wire to the other end, and the plates immersed in dilute sulphuric acid; the galvanometer needle will indicate a current proceeding from the iron through the liquid to the copper, because the iron is attacked by the acid and the copper is not. Now let the plates be taken out of the acid, washed in water, and then immersed in an aqueous solution of sulphide of potassium; the needle will immediately move the contrary way, showing that the current is reversed, and that the copper is now the positive metal.

Mere dilution of the liquid is sometimes sufficient to reverse the current. The following table contains two columns in which the same metals are written one above the other, in such order that each metal is positive, or determines the direction of the current, with all those which precede it in the same column, the exciting liquid being strong nitric acid for the metals in the first column and dilute nitric acid for those in the second. It will be seen that the order of the metals is not the same in the two columns, but in all cases the direction of the current is determined by the metal which is most attacked:—

*Strong Nitric Acid.*

Oxidised iron  
Silver  
Mercury  
Lead  
Copper  
Iron  
Zinc  
Tin.

*Dilute Nitric Acid.*

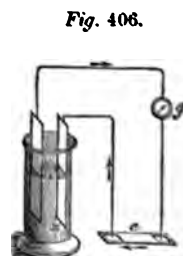
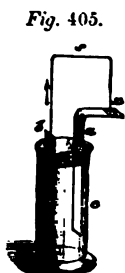
Silver  
Copper  
Oxidised iron  
Iron  
Lead  
Mercury  
Tin  
Zinc.

The next table gives the results of Faraday's experiments with seven different liquids. It is arranged like the preceding, each metal being positive with regard to all those above it when acted upon by the liquid at the head of the column. The numbers in each column indicate the order in which the metals follow each other when the exciting liquid is a dilute acid:

Nitric acid, dilute.	Sulphuric acid, dilute.	Hydrochloric acid.	Nitric acid, concentrated.	Solution of caustic potash.	Sulphhydrate of potassium, colourless.	Sulphhydrate of potassium, coloured.
1. Silver	1. Silver	3. Antimony	5. Nickel	1. Silver	6. Iron	6. Iron
2. Copper	2. Copper	1. Silver	1. Silver	5. Nickel	5. Nickel	5. Nickel
3. Antimony	3. Antimony	5. Nickel	3. Antimony	2. Copper	4. Bismuth	4. Bismuth
4. Bismuth	4. Bismuth	4. Bismuth	2. Copper	6. Iron	8. Lead	3. Antimony
5. Nickel	5. Nickel	2. Copper	4. Bismuth	4. Bismuth	1. Silver	8. Lead
6. Iron	6. Iron	6. Iron	6. Iron	8. Lead	3. Antimony	1. Silver
7. Tin	8. Lead	8. Lead	7. Tin	3. Antimony	7. Tin	7. Tin
8. Lead	7. Tin	7. Tin	8. Lead	9. Cadmium	2. Copper	9. Cadmium
9. Cadmium	9. Cadmium	9. Cadmium	10. Zinc	7. Tin	10. Zinc	2. Copper
10. Zinc	10. Zinc	10. Zinc	9. Cadmium	10. Zinc	9. Cadmium	10. Zinc

The unvarying relation between the direction of the current and the relative force of the action exerted by the liquid on the two metals is quite sufficient to show that chemical action, and not contact of dissimilar metals, is the source of the electric excitement. A further and convincing proof of this statement is however afforded by

the fact, that a current capable of producing electrolytic decomposition may be obtained without any metallic contact. This is shown by the following arrangement (*Fig. 405*), devised by Faraday. A plate of platinum, *b*, and a plate of zinc, *a*, bent horizontally in the upper part, are immersed in water acidulated with sulphuric acid; a piece of filtering paper moistened with iodide of potassium solution is laid on the zinc at *x*, and a platinum wire attached to the plate *b* is brought down to the upper surface of the moistened paper *without touching the zinc*. Immediately a brown spot of iodine shows itself on the upper surface of the paper at *x*, while the lower surface remains uncoloured, showing that the iodine is separated at the extremity of the conductor from which the  $+E$  enters the solution, just as in the decomposition effected by the current of the electrical machine (*p. 397*). Here then we have additional evidence of a current in which the  $+E$  passes from the zinc through the wire to the platinum, and then round the external conductors to the zinc. If the arrangement be somewhat modified so as to introduce a galvanometer, as at *g* (*Fig. 406*), the deflection of the needle will indicate the same direction of the current. The effects are the same when a solution of potash is substituted for the dilute acid as the exciting fluid.



The strength of the current in these and all other voltaic circuits, depends partly on the exciting or "electro-motive" force, resulting from the action of the liquid on the zinc or other metal of the couple, partly on the resistance which the current meets with in the different parts of the circuit. In the particular arrangements now under consideration, in which the resistance offered by the conducting wire and other metallic parts of the circuit, is constant, the force of the current depends upon the relation between the electromotive force of the couple, and the resistance of the solution at *x* which is decomposed by the current. If the affinity between the elements of this liquid—the "electrolyte"—is too great to be overcome by the electromotive force of the couple, the current is arrested and the galvanometer needle returns to its natural position. Different electrolytes offer very different degrees of resistance to decomposition, and consequently some are decomposed by a given electromotive force, while others are not: thus a couple composed of zinc, dilute acid and platinum will decompose solution of iodide of potassium and fused chloride of silver, but not acidulated water. Hydrochloric acid, fused nitrate of silver, or fused iodide or chloride of lead likewise resist the electromotive force of the same couple, with dilute sulphuric acid as the exciting liquid, but are decomposed on adding a small quantity of nitric acid to this liquid, which increases its chemical action on the zinc.

The following table contains the results of a number of experiments by Faraday on the power of different voltaic couples in decomposing various electrolytes. Each horizontal line of this table contains the names of the four substances comprised in a circuit; the last column exhibits the comparative strength of the current, as indicated by the galvanometer:—

Active metal.	Exciting liquid.	Inactive metal.	Electrolyte decomposed.	Character of current.
Iron .	Dilute nitric acid .	Platinum	Sulphide of potassium	Full current
" .	" " .	"	Red nitric acid .	"
" .	" " .	"	Pale strong nitric acid	Good
" .	" " .	"	Green nitrous acid .	Very strong
" .	" " .	"	Iodide of potassium .	Full
" .	Dilute sulphuric acid	"	Sulphide of potassium	"
" .	" " " "	"	Red nitric acid .	Good
" .	Hydrochloric acid .	"	Green nitrous acid .	Very strong
" .	" " dilute .	"	Red nitric acid .	Good
" .	" " " "	"	Sulphide of potassium	"
" .	Solution of common salt	"	Green nitrous acid .	Very strong
" .	Ordinary water .	"	" " " "	Good
Zinc .	Dilute nitric acid .	"	Iodide of potassium .	"
" .	Hydrochloric acid .	"	" " " "	"



Active metal.	Exciting liquid.	Inactive metal.	Electrolyte decomposed	Character of current.
Cadmium	Dilute nitric acid	Platinum	Iodide of potassium	Good
"	Hydrochloric acid	"	"	"
Lead	Dilute nitric acid	"	"	"
"	Hydrochloric acid	"	"	"
Copper	Dilute nitric acid	"	"	"
"	Hydrochloric acid	"	"	"
Lead	Strong sulphuric acid	Iron	Dilute sulphuric acid	Strong
Tin	"	Platinum	"	"
Copper	Sulphide of potassium	"	Dilute nitric acid	"
"	"	"	Iodide of potassium	"
"	Strong nitric acid	Iron	Dilute nitric acid	Very strong
"	"	"	Iodide of potassium	"
Silver	"	"	Dilute nitric acid	Strong
"	"	"	Iodide of potassium	Good
"	Sulphide of potassium	"	Dilute nitric acid	Strong
Tin	Strong sulphuric acid	Copper	Dilute sulphuric acid	"

The liquid which unites the two metals of the voltaic couple likewise suffers decomposition during the whole time that the current is passing, and its elements are transferred in opposite directions, one to the active the other to the inactive metal. In fact, the exciting liquid is itself an electrolyte, and it is only a liquid capable of decomposing in this way that can act as the exciter of a voltaic couple, the decomposition which it undergoes being exactly similar to that which the current produces in any other electrolyte through which it passes; in the one part of the circuit as in the other, one set of elements, the electro-negative or chlorous elements, Cl, Br, I, O, S, SO<sup>4</sup>, NO<sup>3</sup>, &c., are transferred in the direction of the current of  $-E$ , and the others, the electro-positive or basylous elements, viz. hydrogen and the metals, in the direction of the current of  $+E$  (pp. 397, 432).

In all the combinations mentioned in the preceding table, it will be found that, during all the time the current is passing, hydrogen is continually evolved from the liquid in the acting cell, at the surface of the inactive or negative metal, and at the same time the zinc or other active metal unites with chlorine, sulphur, SO<sup>4</sup>, NO<sup>3</sup>, &c., according to the nature of the exciting liquid, and dissolves. No evidence of commotion or action of any kind can be detected in any part of the liquid, excepting at the surface of the metallic plates; but as one of the elements is being continually transferred to the active and the other to the inactive metal, it is clear that a continued movement and shifting of particles must be going on. The nature of this movement we have now to examine; but first it must be observed that the active metal of a voltaic couple is usually subject to two kinds of action, one of which is essentially connected with the formation of a current, while the other is independent of it.

When a piece of ordinary commercial zinc is immersed in dilute sulphuric or hydrochloric acid, it immediately begins to dissolve and hydrogen is evolved upon its whole surface. Now let a plate of platinum or copper be immersed in the same liquid, and either brought in direct contact with the zinc under the liquid, or connected with it by a wire; immediately the greater part of the hydrogen is evolved at the surface of the latter metal, although this metal undergoes no change, and the zinc dissolves faster than before.

The effect of the inactive metal is still more striking when pure zinc, freed from foreign metals by redistillation, is used. A plate of this pure zinc immersed in dilute acid remains quite inactive, no gas being evolved at its surface; but as soon as a plate of copper or platinum is brought in contact with it, a brisk action is set up, the zinc dissolves, and hydrogen is evolved from the surface of the copper or platinum. It would appear from this that the establishment of an electric current is an essential condition to the solution of the zinc. When the zinc contains foreign metals, such as iron, lead, &c., these metals act just like an immersed plate of copper or platinum, establishing local currents within the liquid; and after the action has gone on for some time, these metals, especially the lead, are seen to separate from the surface in filaments. When, therefore, impure zinc (or other metal) is used to form the active metal of a voltaic couple, two kinds of action take place together, the solution of one part of the zinc being essentially related to the current which is established between the elements of the couple, and that of the rest depending on the so-called *local action*, due to the

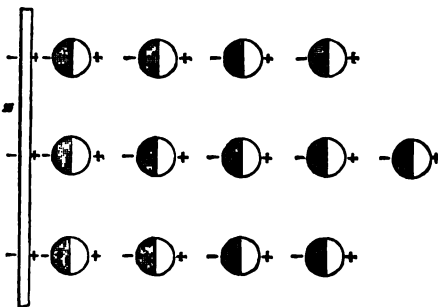
presence of the foreign metals in the zinc. On making the connection between the two metals, the local action on the zinc is greatly diminished in amount, but does not cease altogether. Hence it follows that pure zinc is more advantageous for use in a voltaic couple than the impure metal, because a certain portion of the latter always dissolves without contributing to the production of the electric current.

Ordinary zinc may, however, be made to act with acids in exactly the same manner as distilled zinc, by amalgamating its surface with mercury. This is easily done by rubbing the surface with a rag dipped in dilute sulphuric acid, and at the same time spreading the mercury over it. The zinc then becomes uniformly amalgamated, not only on its surface, but right through, unless the plate is very thick. A plate of zinc thus amalgamated shows no signs of action when simply immersed in dilute acid; but on connecting it with a plate of copper or platinum, as above, hydrogen is briskly evolved from the surface of the latter metal, and the zinc dissolves. The mercury appears to act, partly by rendering the surface uniform, and removing the metallic impurities on which the local action depends, partly in a manner to be presently noticed (p. 420).

*Theory of the Voltaic Couple.*—The remarkable fact that a piece of pure zinc or of amalgamated zinc exerts no decomposing action on water or dilute acids when alone, but acts immediately on being connected with another metal not itself acted upon by the liquid, seems at first sight to favour the supposition that the action begins at the surface of contact of the two metals, and is essentially dependent upon that contact. The effect is, however, exactly the same when no actual metallic contact takes place, as when the conducting circuit is completed by the intervention of an electrolyte (p. 417). The zinc then dissolves, and hydrogen is evolved at the surface of the platinum as long as the current passes, but no longer.

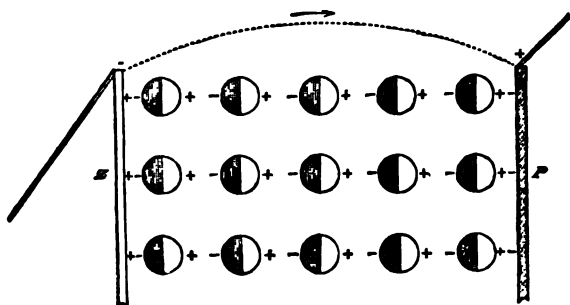
Now we have seen (p. 404) that an electric current may be regarded as a succession of charges and discharges taking place throughout a series of polarised molecules; accordingly, the state of things in the voltaic couple may be represented as follows: Suppose a plate of pure zinc, *Z* (fig. 407), to be immersed in hydrochloric acid. We may suppose that its particles polarise those of the acid which are in contact with them, in the manner shown in the figure, the atoms of chlorine becoming negative and turning towards the surface of the zinc, which becomes positive, while the atoms of hydrogen become positive and turn the contrary way. These molecules then polarise the next in a similar manner, these the next, and so on. At the same time the atoms of the zinc itself become oppositely polarised, each turning its positive pole towards the liquid, and its negative pole the other way; or probably the two elementary atoms in each molecule of the zinc (i. 187) are thrown into opposite electrical states.

Fig. 407.



When a plate of an inactive metal, such as platinum, is introduced into the same liquid as at *P* (fig. 408), its particles become polarised in like manner by the influence of the already polarised molecules of the liquid, turning their negative poles towards the liquid and their positive poles outwards. This state of tension continues till one of the plates, say *Z*, is connected with the earth. The negative electricity is then discharged, and on connecting *P* with a condensing electroscope, the + *E* shows itself. At the same time, the chlorine of the molecule of acid in contact with the zinc

Fig. 408.





unites with it, their opposite electricities being thereby neutralised; the hydrogen of the first particle of acid unites with the chlorine of the second, the hydrogen of this with

Fig. 409.



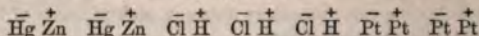
the chlorine of the third, and so on, till the hydrogen in contact with the inactive metal *P*, finding no chlorine to unite with it, is either set free, or more frequently, as the action in this state of tension of the couple is very slow, remains attached to the surface of the platinum plate.\* This action goes on only till the tension of the charge on the insulated plate becomes strong enough to cause the two electricities to recombine across the liquid; and as the whole arrangement consists of conducting materials, the tension thus attained must necessarily be very low, and accordingly, the amount of chemical action which takes place is but slight; but on connecting the two plates by a wire or other good conductor, the particles of that conductor also become polarised, a regular series of charges and discharges taking place along it, as well as in the two metals, *Z*, *P*, and the intervening liquid. The action, therefore, becomes continuous, the atoms of chlorine being transferred towards the zinc, and those of the hydrogen in the opposite direction to the platinum, where they escape.

A precisely similar explanation will apply to every case of the development of electricity by a combination of two metals, and a liquid which acts chemically on one of them. The liquid must be an electrolyte, that is, a compound whose elements can be transferred in opposite directions, like those of the hydrochloric acid, *e. g.*  $\overset{+}{\text{H}}\overset{-}{\text{O}}$ ,  $\overset{+}{\text{H}}\overset{-}{\text{S}}\overset{-}{\text{O}}_4$ ,  $\overset{+}{\text{H}}\overset{-}{\text{N}}\overset{-}{\text{O}}_3$ ,  $\overset{+}{\text{Cu}}\overset{-}{\text{Cl}}$ ,  $\overset{+}{\text{Cu}}\overset{-}{\text{S}}\overset{-}{\text{O}}_4$ ,  $\overset{+}{\text{Pb}}\overset{-}{\text{I}}$ ,  $\overset{+}{\text{K}}\overset{-}{\text{S}}$ , &c. The liquid state is evidently essential to the molecular transference.

The local action which takes place when zinc containing foreign metals is immersed in an acid, may be explained thus. Suppose *Z* (fig. 409) to be a plate of zinc, with here and there a particle of iron, *F*, on its surface. Local currents will then be established between different parts of the surface, the zinc forming the active, and the iron the inactive metal,

and between them polar chains of molecules will be formed, just as when a plate of another metal is placed in connection with the zinc.

The effect of amalgamating the zinc is partly, as already observed, to remove the foreign metals, partly, also, to enable the atoms of the zinc to polarise more regularly: for in a molecule of the amalgam,  $\text{ZnHg}$ , the atoms of zinc and mercury take up the opposite polar states more easily than the two atoms of zinc in a compound molecule of the metal,  $\text{ZnZn}$ ; and moreover, the semi-fluid condition of the amalgam enables the molecules to turn their poles easily in the direction which the polarising action tends to give them. The arrangement of a series of molecules of amalgamated zinc, hydrochloric acid, and platinum may be thus represented:



The precipitation of one metal from its solution by another, as of copper by iron, lead by zinc, silver by mercury, &c., affords an example of a simple voltaic circuit. When a piece of common zinc is immersed in a solution of acetate of lead, local currents are set up in the manner just explained, and the effect of such a current passing through the solution, is to precipitate a particle of lead on a point of the surface of the zinc, where a particle of any foreign metal, such as lead or iron, happens to be situated; the lead thus deposited forms a more distinct inactive or negative metal, and thus an increased electrolytic action is set up, more lead being precipitated on the surface of the first portion; and in this manner fresh particles of lead continually attach themselves to those previously deposited, the precipitated metal taking the well-known arborescent form called the lead-tree, or *Arbor Saturni*. Similarly, when iron is immersed in a solution of copper, there are always a few oxidised points, or small particles of carbon, on certain points of the surface, which favour the formation of local currents, and thereby determine the precipitation of the copper. The precipitation is of course greatly facilitated in the first instance by bringing the precipitating metal in contact with

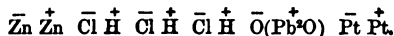
\* When a platinum plate which has thus been used, is placed in acidulated water, together with a clean platinum plate in its ordinary state, and the two connected with a galvanometer, the needle indicates the existence of a current, in which the first plate of platinum is the active metal. This effect is due to the film of hydrogen adhering to it, which in fact makes it act like a plate of zinc. (De la Rive.)



another which is not acted upon by the liquid, and in this manner many metallic precipitations may be effected, which would not otherwise take place. Thus, silver does not of itself precipitate copper; but on touching the silver under the liquid with a piece of iron, a current is immediately established in which the iron forms the positive, and the silver the negative metal, and the copper is then precipitated on the silver.

The protection of one metal from the action of a liquid by bringing it in contact with another, is also a case of the formation of a simple voltaic circuit; such was the method proposed by Davy for protecting the copper sheathing of ships by attaching to it pieces of a more oxidable metal, such as zinc. The zinc then formed the positive and the copper the negative metal, and consequently the oxygen and chlorine of the sea-water were directed to the zinc, instead of to the copper. The galvanising of iron by uniting it with zinc is another example of this mode of action. On the other hand, the corrosion of a metal by the action of air and water is sometimes accelerated by contact with another less oxidable than itself; thus iron railings are often found much corroded near their lower ends, where the iron is in contact with the lead which has been run in to fix it in the stone.

When the liquid in a voltaic combination acts in a similar manner on both the metals, *e.g.* when zinc and copper are immersed in nitric acid, the electric tension and current produced are such as result from the difference of the polarising actions exerted by the two metals on the liquid; if these actions are equal, as when two plates of the same metal are immersed in an acid, no current is produced. If, on the other hand, one of the metals or other conductors has an affinity for the positive element of the electrolyte, *i.e.* for the hydrogen if the electrolyte is an acid, while the other tends to unite with the negative element of the electrolyte, it is easy to see that the molecules of the electrolyte will be polarised by the sum of these two forces, and thus a much stronger current or a higher electric tension will be produced. Such a combination may be formed by zinc, acidulated water, and a plate of platinum covered with peroxide of lead; here the negative element of the acid ( $\text{Cl}$  or  $\text{SO}^+$ ) tends to unite with the zinc, and the oxygen of the peroxide with the hydrogen of the acid, and the polarisation may be thus represented:



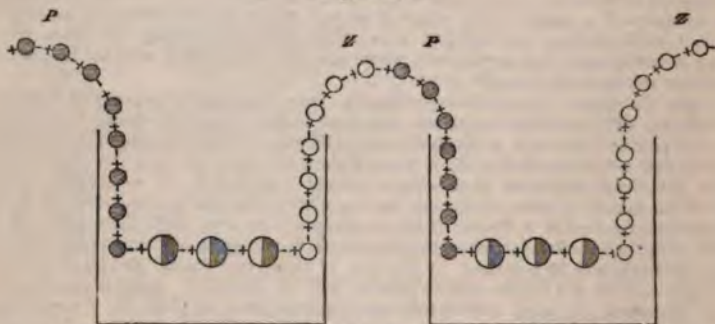
This combination charges the condenser and deflects the galvanometer much more strongly than the ordinary combination of zinc, acid, and platinum. A convenient way of forming it is to pack a quantity of the dry finely powdered peroxide into a rectangular cell of porous earthenware (such as those used for Grove's battery), introduce a thin plate of platinum having a wire soldered to it into the middle of this cell, so that it may be completely enveloped by the peroxide, and immerse the porous cell thus filled, together with a plate of amalgamated zinc, in an acid or saline solution. On connecting the zinc and platinum plates with two platinum wires terminating in acidulated water, the water is quickly decomposed, an effect which would not be produced by a single couple of zinc and platinum without the peroxide. The only use of the platinum in this arrangement is to act as a conductor. The strength of the current rapidly diminishes, however, chiefly in consequence of the reduction of the peroxide of lead to protoxide. Peroxide of manganese produces the same effect as peroxide of lead, but less strongly, and with even more rapid diminution. A similar effect, but also less powerful than that with peroxide of lead, is produced when the porous cell is filled with strong nitric acid and a platinum plate is immersed in it. In this, which is Grove's combination, the polarisation resulting from the affinity of the zinc for the chlorine or other negative element of the acid is intensified by that of the external atom of oxygen in the molecule  $\bar{\text{O}}(\text{NO}^+\text{H})$  for the hydrogen.

The tendency of the peroxides of lead and manganese to deoxidation, by taking up the hydrogen of water or acids, is so strong, that very distinct indications of electric action are obtained, either in the state of tension or in the form of a current, on immersing in water a plate of platinum, and peroxide of lead or manganese, either in lumps or in fine powder, spread upon another plate of platinum. The uncovered plate of platinum then yields  $-E$  to the condenser, the peroxide at the same time yielding  $+E$ . On connecting the two plates with a galvanometer, the current of  $+E$  passes from the covered plate through the coil to the uncovered plate; but the current has not sufficient tension to pass through water. The addition of an acid, especially hydrochloric acid, to the liquid, greatly increases the force of the current, by facilitating the oxidation. A platinum wire covered with peroxide of lead and a gold wire, immersed in hydrochloric acid, yield a powerful current, proceeding from the covered platinum externally to the gold, the latter metal dissolving at the same time as chloride. Similar combinations with chromate of potassium, instead of the peroxide, yield very strong currents.

the chromic acid being reduced to chromic oxide. A copper plate oxidised on the surface forms with zinc and dilute sulphuric acid a more powerful current than a plate of clean copper.

**Compound Voltaic Circuit. Voltaic Pile or Battery.** The electric tension produced by a single voltaic couple is very small, because the opposite electricities can easily recombine through the medium of the liquid. It may, however, be increased by uniting a number of such couples together in regular order, the negative metal of the first being connected metallically with the positive of the second; and so on throughout the series. To understand how this increase of tension is attained, consider two couples of zinc, water, and platinum, connected in the manner just described (*fig. 410*). If

*Fig. 410.*



the second couple were inactive, the particles of the zinc, water, and platinum which compose it would be polarised to a certain degree of tension by the influence of the first; but, besides receiving this degree of charge, they likewise become polarised in the same direction, and to an equal degree, by the chemical action of the zinc and water in the second cell. These two actions, therefore, assist each other, and the resulting intensity in the second couple is twice as great as it would be if that couple were disconnected from the first. The polarisation of the second couple is also transmitted to the first, so that both couples have their electromotive force doubled. In like manner, the addition of a third couple will treble the electromotive force; and so for any number.

Hence when the opposite extremities or poles of an insulated voltaic circuit composed of a large number of couples are connected, each with an electroscope, the leaves of the two electroscopes diverge with opposite electricities. Moreover, by testing the different parts of such a series with an electrometer, it is found that when the whole is insulated, the tension of the opposite electricities is greatest at the two poles, and goes on continually diminishing towards the middle, where it is nothing. Now the electric tension of the different parts of the series cannot proceed from the intermediate couples, because the opposite electricities of each pair of zinc and platinum plates neutralise each other; it proceeds, therefore, from the opposite electricities accumulated at the extremities or poles, which are constantly tending to reunite, and are constantly renewed by the chemical action. On connecting one pole with the ground, and thereby discharging one kind of electricity, the tension of the other pole is increased.

The electric tension exhibited by the poles of a voltaic battery depends in a great measure on the nature of the liquid with which the cells are filled. The greatest possible tension would be obtained by an arrangement which should unite great electromotive power with imperfect conduction. Generally, however, the conducting power of a liquid increases with its power of acting chemically on the zinc.

The battery, whether charged with water, acid, or a saline solution, always takes a certain time to attain its maximum tension, that time being greater as the conducting power of the liquid is less; but with very good conductors, such as dilute acids, the maximum tension is attained almost instantly. In all cases, the statical, as well as the dynamical, effects of the battery are essentially dependent on the chemical action between the liquid and the positive metal. The stronger this action, the smaller is the number of couples required to produce a given tension. Gassiot has found that a Grove's battery (to be hereafter described) of 400 cells, well insulated in glass vessels, exhibits at the two poles a tension equal to that of a water battery of 3520 pairs.

The poles of a voltaic battery in a state of tension discharge to each other, just like two metallic rods connected with the positive and negative conductors of an electrical

machine. When the poles of the 400 pairs of Grove's battery, just mentioned, were placed in connection with two copper discs placed at the distance of  $\frac{1}{16}$  of an inch from one another, a rapid succession of sparks was produced.

The wire along which the current of the voltaic battery is passing, either continuously or by intermittent spark-discharge as just described, exhibits the same effects as one which conveys the discharge of an electrical machine or Leyden jar. The wire itself, if not very thick, becomes warm, and a thin wire of platinum interposed in the circuit is heated to redness, or fused, according to the strength of the current; magnets are deflected, and iron and steel magnetised by it; and if the two poles of the battery are connected with two platinum wires or plates immersed in water acidulated with sulphuric acid, the water is decomposed, hydrogen being evolved from the wire connected with the negative pole, and oxygen from that connected with the positive pole. Any of the other electrolytes mentioned on page 397, as decomposed by friction-electricity, may also be decomposed with ease by the current, even of a small voltaic battery. The quantity of oxygen and hydrogen thus evolved in a given time affords, as we shall afterwards more particularly explain, a measure of the quantity of electricity evolved by the battery. Now the *quantity* thus evolved, whether measured by the amount of water or other electrolyte that it will decompose, or by the deflection of a magnetic needle (p. 398), is incomparably greater than that evolved by the most powerful electrical machine; a pair of thin wires of zinc and platinum dipped for a moment into dilute acid will produce a current capable of decomposing a larger quantity of iodide of potassium than could be decomposed by a large electrical machine working for a considerable time.

But the *intensity* of the charge of a voltaic battery, even of a very large number of pairs, is almost immeasurably below that of the electricity produced even by rubbing a piece of glass with the dry hand; in fact, the whole of a voltaic arrangement consists of materials possessed of considerable conducting power, and therefore the neutralisation of the opposite electricities takes place through the battery itself more easily than through even a very small stratum of air, or other insulating body.

The exact relations between the quantity and intensity of the voltaic current will be more fully considered hereafter. At present it may suffice to state that, with a conducting circuit not offering much resistance, the quantity of electricity developed in a given time increases nearly in direct proportion to the size of the plates in a single pair (not to the total extent of metallic surface in the battery), whereas the intensity, or power of overcoming resistance increases, as already observed, directly as the number of pairs. Hence when the current is to pass only through a metallic conductor of no great length—as for most electro-magnetic experiments, and for heating wire not extremely thin—a single pair of plates will act as well as a compound battery, provided all the connections are good. Hare's *calorimotor* for heating wires is an arrangement of this kind. A number of zinc and copper plates are fastened alternately and perpendicularly in a frame, all the copper plates being soldered to one common bar of metal, and all the zinc plates to another, so that the whole acts like a single pair of very large zinc and copper plates. With from 60 to 120 copper and zinc plates, each having a surface of 19 square inches, excited by dilute acid, a platinum wire  $\frac{1}{4}$  of a line thick may be fused. Another mode of obtaining a large surface in a small space is to roll together a zinc and copper plate 6 inches broad and 9 inches long into a cylinder  $2\frac{1}{2}$  inches in diameter, in such a manner that they never come into contact, but are always kept about a quarter of an inch apart. All the copper plates of a number of such rolls are united by soldering with a single metallic rod, and all the zinc plates with another.

*Dry Piles.*—The greatest degree of intensity is obtained by the so-called dry piles, which consist of a great number of pairs of two metals separated by paper instead of a liquid conductor, tinfoil being generally used as the positive, and peroxide of manganese as the negative metal. In these piles, as in the ordinary voltaic battery, the motive power is chemical action, the exciting liquid being the moisture in the paper, the oxygen of which is continually combining with the tin, and the hydrogen with the oxygen of the peroxide of manganese (p. 421); in fact, the pile acts only so long as the paper remains moist, so that the appellation *dry pile* must not be understood in its literal sense.

The best way of constructing a dry pile is to take a sheet of paper tinned on one side, and cover it on the other side with a paste made of peroxide of manganese mixed with milk and starch or gelatin, to make it adhere. The paper thus coated is left to dry, and then punched into a number of small circular discs, which are laid one upon the other in a glass tube, care being taken that the tinned surfaces are all laid the same way; when the tube is quite full, its ends are closed with brass caps, which must be metallically connected with the two extremities of the pile.

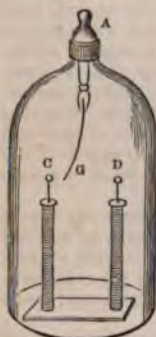
The tin end of such a pile exhibits  $-E$ ; the manganese end,  $+E$ . A pile of



several thousand pairs produces strong divergence of the leaves of an electroscope, when one of its ends is brought in contact with the cap of the instrument, while the other is held in the hand; and, on connecting its two poles by a wire, small sparks are obtained. The pile does not produce a continuous current, since, in consequence of the imperfect conduction of the paper-discs, it takes some time to recover its maximum tension after being discharged. With a dry pile composed of a comparative small number of large discs, some of the dynamic effects of electricity may, however, be obtained; thus Delezenne succeeded in decomposing water with a dry pile composed of 300 pairs, each having a surface of 270 square centimetres.

The chief use of the dry pile is to assist in the construction of a very delicate electroscope, called from its inventor, *Bohnberger's electroscope*. It consists of two

Fig. 411.



dry piles, C, D (fig. 411), placed vertically at a distance of four or five inches, with their poles in opposite directions; and of a single gold leaf, G, suspended just midway between them from a brass rod passing through the cap, A, of a glass receiver which covers the whole arrangement. The poles of the two piles, being charged with opposite electricities, attract the gold leaf in opposite directions, so that, if suspended exactly in the middle between them, it hangs vertically while not itself electrified; but as soon as the slightest charge is communicated to it, it moves towards the pile whose superior pole is charged with the electricity opposite to its own. The instrument is so sensitive that it is affected by an excited rod of glass or sealing wax at the distance of a yard; in fact, it is sometimes too delicate: for if the piles are placed too close together, and the leaf, from any slight disturbance is thrown a little out of the vertical, it will be drawn towards one pile or the other, even though not itself electrified. A pith-ball or a small disc of gilt paper suspended by a silk thread between the opposite poles of two dry piles, oscillates between them as long as the piles continue in action.

A well constructed dry pile will remain active for two or three years; but the action ultimately stops, either from desiccation of the paper, or from formation of a thin film of oxide on the surface of the tin-foil.

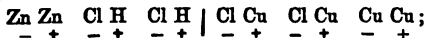
The older forms of the galvanic or voltaic apparatus, viz. the pile of Volta, Cruikshank's trough, and Wollaston's battery, are too well known to need particular description; moreover, they are now but little used. They all consist of a series of couples of zinc and copper, excited by an acid liquid, generally a mixture of water with  $\frac{1}{10}$  of its bulk of sulphuric and  $\frac{1}{60}$  of nitric acid.

**Constant Batteries.**—In all voltaic combinations consisting of two metals and one liquid, the force of the current continually diminishes, in consequence of the alterations which the chemical action produces in its component elements. Consider, for example, the ordinary combination of zinc, sulphuric acid, and copper. As the zinc dissolves, the action of the acid on the remaining metal becomes less energetic, and therefore the electromotive force, which depends upon that action, is diminished. But, besides this, the sulphate of zinc thus produced, and the water, are decomposed by the current, hydrogen and zinc being carried towards the surface of the copper. The zinc is there deposited, and tends to form a counter current, just as if a plate of zinc were substituted for the copper; and the hydrogen likewise diminishes the force of the current, partly by clinging about the surface of the copper, and forming a non-conducting film, which impedes the passage of the current, partly by acting as a positive element, in the same manner as in Grove's gas-battery (p. 430), and thereby also generating a counter-current. When common zinc is used, a further variation arises from the local action induced by the foreign metals present in the zinc, and continually increases as those metals are separated in larger quantity (p. 418). This last inconvenience is completely obviated by the use of amalgamated zinc.

The variation of power arising from the saturation of the acid may be prevented by gradually removing the spent liquid and replacing it with fresh acid, which, however, introduces considerable complication into the arrangement of the battery; this source of variation is greatly diminished by the use of amalgamated zinc, which acts only while the circuit is closed, and therefore does not saturate the acid so quickly.

The variation arising from the transference of zinc and hydrogen to the surface of the negative metal is prevented by immersing that metal in a liquid of different composition from that which acts upon the zinc, and capable of absorbing the hydrogen, the two liquids being separated by a porous partition, which prevents them from mixing, but does not interrupt the electric communication. This object may be effected by various arrangements, the most important of which are the batteries of Daniel, Grove, and Bunsen.

In *Daniell's battery*, each cell consists of a copper cylinder, *cc* within which is placed a cell *ab*, either of porous earthenware or animal membrane, filled with a mixture of 1 measure of strong sulphuric acid and 8 measures of water, and in this is immersed a cylinder of amalgamated zinc *z*. The space between the porous cell and the copper cylinder is filled with a saturated solution of sulphate of copper. On connecting the zinc with the copper by a wire, the zinc dissolves, and the particles of the two liquids become polarised in the manner represented below:



the sulphates, for greater simplicity, being supposed to be replaced by chlorides. The last atom of hydrogen, instead of passing on to the copper, unites with the chlorine of the first atom of chloride of copper beyond the porous diaphragm; the atom of copper thus set free unites with the next atom of chlorine, and so on, till the last molecule of cupric chloride is reached, the copper-atom of which is deposited on the surface of the copper cylinder in the metallic state. Thus the copper, instead of having its surface tarnished by a deposit of zinc, or polarised by adhering hydrogen, is kept continually bright by fresh deposits of metallic copper.

This is the action which goes on in a Daniell's cell, so long as the copper solution remains tolerably well saturated. It is clear, however, that in course of time it must become weak unless renewed; and when it becomes dilute, water is decomposed as well as the cupric salt, and hydrogen then passes on to the copper surface. It is important, therefore, to keep the copper solution saturated; and for this purpose a shelf of perforated copper is fixed round the interior of the copper cylinder at about an inch below its upper edge, and on this shelf are laid crystals of cupric sulphate, which dissolve as fast as the copper is removed from the solution by the action of the current.

A Daniell's battery thus fitted up remains nearly constant for a considerable time; but the acid of course becomes gradually exhausted. To preserve it at a constant strength, the copper cylinder *AB* was originally constructed as shown in *fig. 413*, with a siphon-tube *efg*, proceeding from its lower part and terminating within

Fig. 412.

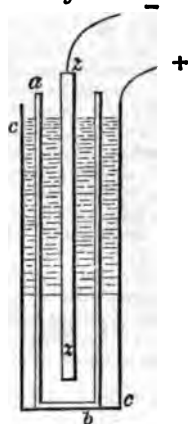


Fig. 413.

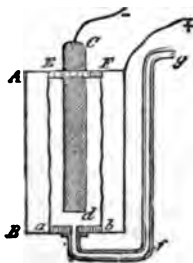
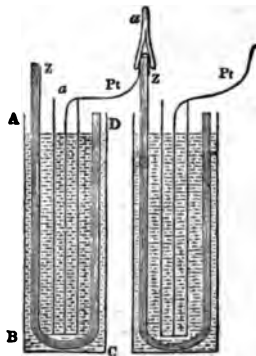


Fig. 414.



the ox-gullet *a b*, *FE*, which formed the porous cylinder. By this tube an outlet was provided for the spent liquid as fresh acid was poured in at the top. This construction has, however, not been found to yield sufficient advantage in point of constancy to compensate for the additional complication which it involves. Buff has contrived a modification of the Daniell's cell, in which the zinc plate or cylinder is sustained by a counterpoise, and allowed gradually to sink in the liquid, thus presenting a greater surface to the action of the acid as that liquid becomes weaker.

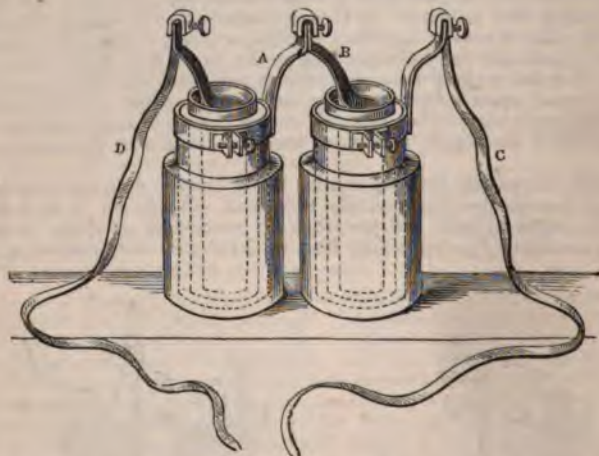
*Grove's battery.*—In this battery (*fig. 414*) the positive-metal consists of amalgamated zinc immersed in sulphuric acid diluted with about 10 times its bulk of water, and the negative metal of platinum immersed in strong nitric acid. Each zinc plate, *Z*, bent



round, as in the figure, is contained in a rectangular vessel of glass or glazed earthenware A B C D, filled with dilute sulphuric acid. Between the two bends of the zinc plate is placed a narrow rectangular cell of porous earthenware, containing strong nitric acid, and in this is immersed a plate of platinum, bent at the top to meet the next zinc plate, against which it is pressed by a small split piece of wood, *a*. The action of this battery is similar to that of Daniell's, but stronger, because the hydrogen evolved by the decomposition of the water is rapidly taken up by the nitric acid, which, in fact, acts upon it like peroxide of lead, or manganese (p. 421), and tends greatly to intensify the polarity induced by the action of the zinc on the sulphuric acid. The battery is not, however, so constant as Daniell's: for the nitric acid is very quickly reduced to lower oxides of nitrogen, and, after the battery has been in action for about an hour, copious red fumes are given off, which cause great annoyance. This inconvenience may be diminished by using weaker nitric acid (acid of 1.40, mixed with half its bulk of water), or by mixing the stronger acid with one-third or one-half its volume of strong sulphuric acid; both these methods render the action less variable: but the former greatly diminishes the force of the current; the latter is, therefore, to be preferred.

*Bunsen's battery* (fig. 415) is the same as Grove's, excepting that the platinum is replaced by compact charcoal or coke. Each couple consists of a hollow cylinder of carbon enclosed in a glass vessel containing nitric acid, and encloses a cell of porous earthenware which contains dilute sulphuric acid, and a cylinder of amalgamated zinc. The upper

Fig. 415.



rim of each carbon cylinder is enclosed by a copper ring, to which is attached a riband of the same metal, serving to connect it with the zinc of the next couple, in the manner shown in the figure.

The carbon for these batteries is obtained as described at p. 760, vol. i. Its conducting power is somewhat less than that of platinum, and consequently the current produced on first closing the circuit is less violent than that of Grove's battery, and, on this account, somewhat more constant.

The platinum in Grove's battery may also be replaced by lead coated with gold or platinum (Callan, *Ann. Ch. Phys.* [3] viii. 28); also by iron rendered passive by immersion in strong nitric acid; iron in its ordinary state may be used as the positive metal, with passive iron as the negative, but amalgamated zinc is better (Schönbein). Callan has obtained good results with amalgamated zinc and cast iron immersed in dilute sulphuric acid, without the use of nitric acid.

The variation in the strength of the current arising from the adhesion of hydrogen to the surface of the negative metal may also be prevented, to a great extent, by covering the surface of that metal with a coating of finely divided platinum or gold. Plates of platinum or silver may be thus coated by immersion in a solution of chloride of platinum or chloride of gold. Metals thus coated with platinum are said to be *platinised*.



*Smee's battery*, which consists of a series of pairs of amalgamated zinc and platinised platinum, immersed in dilute sulphuric acid, produces a current of much greater constancy than might be expected from a battery of only one liquid, because the hydrogen does not adhere to the rough surface of the platinised platinum. The form of the plates is similar to that adopted in Grove's battery, the plates of zinc being bent double, and the platinum plates interposed between the two surfaces formed by the bend; but as there is only one liquid, and no porous cell, the two surfaces of each zinc plate may be brought much nearer to each other than in Grove's battery. The battery is charged with a mixture of 1 pt. sulphuric acid to 7 pts. water. The plates are attached to a frame, by which they can be easily lifted out of the trough when not required to act.

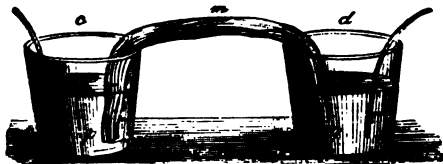
Platinised silver may be used instead of platinised platinum, but silver is not very easily platinised, on account of the high polish of its surface.

None of the forms of battery above described are capable of yielding a really constant current. Daniell's construction gives the nearest approach to constancy; but even in this, variations must arise, as it is impossible to keep the acid at a perfectly uniform strength. The only way of obtaining a perfectly constant current, is to interpose in the circuit, a conductor, the resistance of which can be made to vary inversely as the strength of the action in the battery. The mode of effecting this will be described hereafter (p. 464).

## 2. Development of Electricity by the Chemical Action of Solutions one upon the other.

When two conducting liquids act upon one another, a development of electricity takes place, the more acid liquid becoming positive, and the more alkaline liquid negative. This may be shown by plunging two perfectly clean plates

Fig. 416.



of platinum, connected with the ends of a galvanometer wire, one in nitric acid contained in a glass vessel *d* (fig. 416), the other in a solution of potash contained in another glass vessel *c*, and connecting the two liquids by means of a bundle of cotton or asbestos fibres *p m q*, steeped in a slightly acid or saline solution. The acid and alkali then rise through the bundle of fibres, by capillarity, and as soon as they mix, a current is produced, the  $+E$  passing from the acid through the galvanometer to the alkali. That this effect is really due to the mutual action of the acid and alkali, and not, as Davy supposed, to the different action of the two liquids on the platinum plates, may be proved by immersing the two plates in cups containing a solution of nitre, connecting these two cups by means of a bundle of asbestos or cotton fibres, one with the nitric acid, the other with the potash, and the acid and alkali by another bundle of asbestos as before. The current is then produced in the same direction as with the former arrangement, but somewhat weaker, on account of the small conducting power of the nitre solution. Another mode of operating, so as to obviate the objection above-mentioned, is to plunge the two platinum plates attached to the galvanometer coil into vessels containing nitric acid, connect these vessels by a bundle of cotton fibres about four inches long, moistened with water, then drop gently, by means of a tube, a small quantity of acid and of potash solution near the middle of the cotton. As long as these drops of liquid remain separate, no current is formed; but as soon as they mix, a current is produced in the same direction as in the preceding experiments, the  $+E$  passing from the alkali to the acid, and thence through the connecting wire to the alkali again.

If, in the first arrangement, the cotton or asbestos is moistened with a strong solution of any salt, such as chloride or sulphate of sodium, a current is at first formed by the action of this solution on the acid and on the alkali; this current is, however, comparatively feeble, and is soon succeeded by the stronger current resulting from the mixture of the acid and alkali. Thus, nitric acid and potash connected by cotton containing sulphate of sodium, produced, at first, a deflection of  $4^\circ$  or  $5^\circ$  in the galvanometer, but after a few seconds a deflection of  $20^\circ$ , which remained constant.

Electric currents are also produced by the action of one acid upon another; thus, when strong sulphuric acid is carefully poured into one branch of a U-tube (fig. 417), and nitric acid into the other, so that the two liquids may meet in *m*, without mixing, and the platinum terminals *a b* of a galvanometer are made to dip into

the two acids, a current is formed, in which the  $+E$  passes from the nitric acid directly

Fig. 417.



to the sulphuric acid, and thence through the galvanometer back to the nitric acid, the latter acting, in fact, as a base to the sulphuric acid. Phosphoric acid acts with nitric acid in the same way as sulphuric acid, and with sulphuric acid in the same manner as the latter acts with nitric acid.

Of the conducting solutions in the following series, each is *negative* with those which follow, and *positive* with those which precede it; the term *positive* being here, as before, applied to the body from which the  $+E$  passes directly to the others:

*Phosphoric acid, sulphuric acid, nitric acid, hydrochloric acid, acetic acid, saline solutions, alkaline solutions.*

Water is for the most part positive with acids and negative with alkalis.

In all arrangements like those above described, it is of great importance to clean the platinum plates before each experiment, by heating them to redness, then immersing them in boiling nitric acid, and, lastly, washing them in distilled water. They should then be tested by connecting them with a galvanometer, and immersing them in the same liquid—nitric acid, for example. If quite clean, they will produce no current; if, on the other hand, the needle is deflected, it may be concluded that the plates are *polarised*, by the deposition of a film of oxygen gas on the one, and hydrogen on the other, these gases resulting from the electrolytic action which has taken place in the liquids in which the plates were previously immersed (see the next section). The effect of these gaseous deposits is to produce a current in the direction inverse to that of the current by which they have been formed, and this current may diminish, or even completely neutralise, that which it is desired to produce.

To obviate this source of error, Becquerel contrived an apparatus called a *depolariser*, consisting of a mechanical arrangement by which each of the platinum plates is lifted out of the solution in which it has been immersed, and plunged into the other, their connections with the galvanometer remaining, however, unchanged. The result of this continual shifting of the plates is, that neither of them remains in either of the liquids long enough to become polarised, and therefore the secondary current above-mentioned is not produced. By means of this apparatus, Becquerel has been able to detect the production of a current by the mutual action of liquids, in many cases in which it would not otherwise have been apparent.

Fig. 418.



The intensity of the current produced by the mutual action of liquids may, of course, be increased by joining several couples together, the two liquids in each cell being separated by a porous diaphragm, or, if they differ greatly in density, simply laid one upon the other. The couples are connected by wires of copper or platinum, the extremities of which dip into the positive liquid of one cell and the negative of the next.

A very remarkable form of couple, composed of two liquids and one metal, is that which is known as *Becquerel's Oxygen-circuit*. *CD* (fig. 418) is a glass bottle, into the neck of which is inserted a glass tube *AB*, kept in its place by a cork. Over the bottom of the tube *B* is tied a piece of linen, on which is placed a layer of moist clay, about half an inch thick, and on this is laid a piece of cotton-wool, to prevent it from mixing with the supernatant liquid. The bottle is filled with nitric acid, the tube with solution of caustic potash. The two liquids come into contact through the moist clay, and are also connected by means of a wire, which may be that of a galvanometer, terminating in two plates of platinum *P* *N*, the former immersed in the potash, the latter in the nitric acid. On making this connection, a strong current is produced, the  $+E$  passing from *N* along the wire to *P*, and at the same time the water of the potash solution is decomposed, its oxygen escaping in bubbles at *P*, while the hydrogen is transferred to the nitric acid, which it partly reduces to nitrous acid, thereby colouring the liquid around it red or green.

The current produced by this oxygen-circuit is of constant strength, because the plates do not become polarised; in fact, although the nitrate of potassium formed by the union of the acid and alkali is decomposed by the current, the acid being transferred to the plate *P*, and the alkali to *N*, the acid is immediately neutralised by the potash at *P*, and the alkali by the nitric acid at *N*, so that they

do not remain attached to the plates. This arrangement was the earliest form of a constant voltaic current. Its power may be considerably increased by making the plate *P* of amalgamated zinc instead of platinum; the zinc takes hold of the oxygen, and produces an electric polarisation in the same direction as that resulting from the mutual action of the acid and alkali. A single couple thus constituted decomposes water with facility, and by uniting several such couples a powerful battery is obtained.

*Electricity developed by Decomposition of Solutions.*—When water holding any substance in solution is evaporated in a platinum vessel placed on the plate of a condensing electroscope, the metallic vessel acquires a positive charge when the solution is alkaline, and negative when it is acid, the opposite electricity being in each case carried off by the water. A solution of ammonia forms, however, an exception to the general behaviour of alkaline liquids, because the ammonia, being more volatile than the water, carries off the  $+E$ , and leaves the water negative. To exhibit these effects the evaporation must be rapid, otherwise the opposite electricities have time to recombine. A convenient apparatus for the purpose is a small wide platinum capsule, or a thick piece of platinum foil, slightly hollowed out in the middle. This is to be connected with the lower plate of the condenser, then heated to redness, and a few drops of the solution poured into it. A comparative experiment should first be made with pure water to ensure that there is no electricity developed by the friction of minute globules of water against the edge of the vessel. Peltier has observed, that the development of electricity in these experiments does not take place during the whole time of the evaporation, but only at the moment when the liquid, quitting the spheroidal state into which it has been thrown by contact with the hot metal, experiences a kind of crepitation; he thence concludes that the electric excitement is due to the separation of combined water, and not to the mere evaporation of the water which holds the substance in solution.

### 3. Development of Electricity by the mutual Action of Gases and Liquids. *Polarisation; Gas-Batteries.*

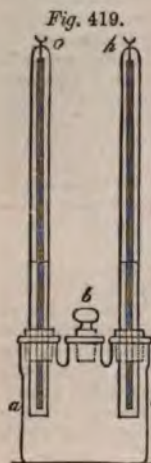
We have already had occasion to notice several instances in which the current produced by a voltaic couple is weakened, or even neutralised, by the action of films of liquid or gas attaching themselves to the surfaces of the solid elements. This kind of action was first observed by Ritter, who found that a pile composed of a number of discs of the same metal, separated by pieces of moistened cloth, though inactive of itself, acquired, by connection for a few seconds, with the poles of an ordinary voltaic battery, a kind of *secondary polarity*, which enabled it for a short time afterwards to exhibit electric tension at its extremities, and produce a current capable of decomposing water. This effect, as pointed out by Volta, is due to the decomposition of the liquid between the metallic discs, resulting from the battery-current sent through it, whereby, if the discs are moistened with a saline solution, acid is transferred towards the end of the pile connected with the positive pole of the battery, and alkali in the contrary direction, so that one surface of each of the metallic discs becomes covered with acid, and the other with alkali. Hence, as already shown, a current is produced, in which  $+E$  passes from the alkali to the acid, that is to say, in the opposite direction to that of the original current. This so-called *polarisation* of metallic surfaces may be produced on a single pair of platinum plates by immersing them in a saline solution, and sending a current through it for a short time; if the current be then stopped, and the plates, while still immersed in the liquid, connected with the ends of a galvanometer coil, a strong inverse current will be produced, lasting for several seconds. The same effect may be produced, without the intervention of electrolysis, by simply immersing one of the plates in acid, the other in alkali, then connecting them with a galvanometer, and plunging them into a conducting solution.

Plates of platinum become polarised in a similar manner, when immersed in water either pure or acidulated, and connected with the poles of a battery, the effect, in this case, being due to the films of hydrogen and oxygen which collect on the negative and positive plates respectively. That this is the true explanation of the phenomenon, is shown by the following facts:—1. The polarity of the platinum plates is destroyed by heating them to redness. 2. When the plate which has been connected with the positive pole of the battery is introduced into a graduated tube filled with hydrogen, and the other into a tube filled with oxygen, both gases are gradually absorbed, the hydrogen disappearing twice as fast as the oxygen. 3. The polarisation of the platinum plates may be produced without the aid of electrolytic action, by simply immersing one of them in hydrogen, and the other in oxygen gas. On subsequently connecting the plates with a galvanometer, and then plunging them into water, a strong current is obtained, the  $+E$  passing from the plate which has been immersed

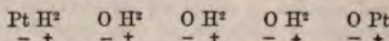


in the hydrogen, through the liquid, to the plate which has been immersed in the oxygen.

*Grove's Gas-battery.*—The secondary currents produced by polarised plates, as above described, are but of short duration; but Grove has succeeded, by a peculiar arrangement founded on the same principles, in producing a continuous current. Two glass tubes (*fig. 419*), closed at top, and each containing a plate of platinised platinum (p. 426), connected with a platinum wire passing through the top, are filled with acidulated water, and supported in a glass vessel, *a a*, also filled with acidulated water. One of the tubes is then filled with oxygen gas, and the other with hydrogen, and the external wires *g, h*, are connected with a galvanometer. A strong current is then produced, proceeding from the hydrogen plate, through the liquid, to the oxygen plate, and at the same time the gases in the tubes gradually disappear, the hydrogen twice as fast as the oxygen. By connecting a number of such pairs together, the hydrogen plate of the one with the oxygen plate of the next, a "gas-battery" is obtained, capable of giving sparks and shocks, decomposing water, &c.



The exciting action in this battery takes place at the surfaces of contact of the platinum, the liquid, and the gases. The hydrogen adhering to the surface of the platinum, in the line of contact between that surface and the liquid, polarises the particles of the liquid, so that the oxygen-atom of each molecule of water is turned towards it, and the hydrogen-atoms the other way—in short, it acts just like the zinc in the ordinary battery. Moreover, the oxygen in contact with the platinum in the other tube polarises the molecules of water in the same direction, and thus the intensity of the action is doubled. The polarisation of a chain of particles may be thus represented:



On making a connection between the two platinum plates, the  $-E$  of the one unites with the  $+E$  of the other; the free hydrogen in contact with the first unites with the oxygen of the adjacent molecule of water, the hydrogen of this with the next, and so throughout the series.

The use of platinised platinum in this battery is not absolutely necessary, as clean polished plates of the metal act in the same way; but the platinised platinum acts more powerfully on account of the greater surface which it affords. Platinum is peculiarly adapted for forming part of such an arrangement, by its medium position on the electrical or chemical scale (p. 13). If an oxidable metal were used, the effect would be complicated by its affinity for the oxygen.

The action of the battery is exactly the same whether the gases which fill the tubes are evolved by the electrolysis of water, or prepared by ordinary chemical methods.

Several other combinations of gases have likewise been tried, viz. chlorine and hydrogen, chlorine and carbonic oxide, oxygen and nitrous oxide, hydrogen and carbonic oxide; but none of them are well adapted for actual use in the battery. Chlorine and hydrogen give a powerful current; but the rapid absorption of the chlorine soon puts a stop to the action. Chlorine and oxygen on the one side, and hydrogen and carbonic oxide on the other, are the only gases which appear to be capable of producing a continuous current in the same manner as hydrogen and oxygen. The other combinations produce no effect after the first few minutes.

*Passive state of metals.*—When a piece of clean iron wire is immersed in nitric acid together with platinum, the latter being introduced first, and the two connected with a galvanometer, a powerful current is formed at the first instant, the iron forming the positive metal; but the strength of the current quickly falls to a very small amount, at which it may remain constant for several days. This effect is evidently due to the formation of a thin coating of oxide. The iron thus treated is no longer attacked by strong nitric acid, but may be preserved in it for any length of time without change; in this state it is said to be *passive*. When an iron wire in this state is immersed in nitric acid, and another iron wire brought in contact with it, and then dipped into the acid, this wire is likewise rendered passive, forming in fact the positive metal of a voltaic couple, in which the first wire is the negative metal. In like manner, a third wire may be rendered passive by connection with the second, and so on. Iron may also be rendered passive by mere immersion in very strong nitric acid, or by holding it for a few seconds in the flame of a spirit-lamp, whereby it becomes superficially

oxidised; or again, by holding the extremity of the wire for a short time in the lamp-flame, and then dipping it gradually into nitric acid, the oxidised end first.

Iron thus rendered passive may be restored to its ordinary state by any treatment which removes the superficial coating of oxide, *e. g.* by touching it while immersed in acid with a piece of ordinary iron, or with zinc; or by making it serve for an instant as the negative pole of a voltaic battery in the decomposition of water, so as to cause an evolution of hydrogen upon its surface; also by immersing it in hydrochloric acid, which dissolves off the film of oxide, or even by washing it with water and rubbing it with bibulous paper.

Passive iron, as already observed, has been recommended as a substitute for platinum in Grove's battery; it is not, however, well adapted for the purpose, as the film of oxide on its surface soon becomes reduced.

Other metals, *viz.* silver, copper, tin, aluminium, and especially bismuth, may be brought into the passive state by the methods above described; but the effect is not so marked with any of them as with iron. (Gm. i. 353—362.)

#### 4. Development of Electricity by Combustion.

Combustion, like all other forms of chemical action, is attended with disengagement of electricity. Volta first showed that electricity is evolved in the combustion of carbon; and the phenomenon was afterwards more completely examined by Pouillet, who found that when a cylinder of charcoal, of good conducting power, is set on fire at one end, then placed on a metal plate communicating with a condenser, and blown upon to keep up the combustion in the upper part, the charcoal and the metal on which it rests become charged with  $-E$ , while the carbonic anhydride evolved exhibits  $+E$ , as may be shown by placing over it a metal plate communicating with another condenser. When hydrogen burns in the air or in oxygen gas, the hydrogen becomes negative, and the oxygen, or perhaps the vapour of water formed by the combustion, positive. This may be shown by means of an insulated spiral of platinum wire connected with a condenser, and held first in the middle of the flame, afterwards at a little distance from it. (Pouillet.)

The electric phenomena of combustion are not, however, so simple as would appear from these experiments, especially when the combustion takes the form of flame. In fact, they are complicated by thermo-electric effects, to such an extent in some cases, that many observers have attributed the entire effect to thermo-electric action. Mr. Grove has, however, succeeded in showing that a large portion of the electricity observed is really due to chemical action. Two platinum wires 15 centimetres long and about  $\frac{1}{4}$  millimetre in diameter, are each coiled into a helix at one end, and communicate by their other extremities with a delicate galvanometer. One of the coils is placed entirely within the yellow flame of a spirit-lamp urged by the blow-pipe, near the apex of the blue flame, and the other near the orifice of the jet of air at the base of the blue cone, or root of the flame, the two coils being separated by a distance of 5 or 6 centimetres. The helix at the apex of the blue flame is heated to whiteness, while the other remains at a cherry-red heat. Under these circumstances, the galvanometer indicates a deviation of  $6^\circ$ ; the coil near the orifice acting like the zinc or positive metal in this kind of voltaic couple with respect to the other.

The effect just described is not due to a thermo-electric current produced at the junctions of the copper and platinum-wires, for it is not altered by heating one of these points of junction with a spirit-lamp. Neither is it a thermo-electric current due to the unequal heating of the two coils; for its direction is not changed by moving the coil in the yellow flame to a part in which it is less heated than the other. If the coil near the base of the flame be brought near the one at the apex, the deflection of the needle diminishes; but its direction does not change till the coils are brought very near together, in which case the flame-current is overpowered by the thermo-electric current, whose direction is determined by the coil which is most heated.

When a wire of zinc, iron, or copper is substituted for one of the platinum wires, the current is stronger when the oxidable metal is in the hottest part of the flame and the platinum wire at the base, than in the contrary case, probably because the oxidable wires, being thicker, produce, when introduced into the hot flame, a cooling effect, which facilitates the development of a thermo-electric current in the same direction as the current due to the chemical action going on in the flame.

The effect may be greatly intensified by uniting the action of these two currents. This is effected by forming a piece of platinum foil into a small cone about a centimetre in depth and width, and introducing this cone suspended in a platinum ring into the full flame instead of the platinum coil. The little hollow cone is filled with water, which is renewed from time to time by means of a pipette. With this arrangement, a current is obtained capable of deflecting the galvanometer needle  $20^\circ$  or  $30^\circ$ ,



and in the same direction as in the preceding experiments. When the cone filled with water was placed at the base of the flame and the coil at the apex, the deviation did not exceed  $5^{\circ}$ .

These experiments show that there exists in flame an electric current, not of thermo-electric origin, and such that the platinum at the base of the flame plays the part of the positive metal in the circuit which it forms with the platinum at the apex. (Grove.)

Matteucci attributes the flame-current to the same mode of action as that which takes place in Grove's gas-battery. In fact, in the arrangements above described, one of the platinum wires is in contact with the combustible matter of the flame, viz. hydrogen or vapour of alcohol, the other with the oxygen of the air, and between them is a quantity of aqueous vapour, the particles of which become polarised, and suffer electrolytic decomposition just as those of the water in the gas battery; the direction of the current is in accordance with this view, the platinum immersed in the hydrogen or alcohol-vapour acting as the positive metal. A similar explanation is applicable to the development of electricity in the combustion of charcoal. Matteucci has shown that when pure charcoal burns in dry oxygen gas, no electricity is developed; but when the combustion takes place in moist air or oxygen, an electric current is produced, the vapour of water being as before the electrolyte, and being decomposed by the hot charcoal, just as the water in an ordinary voltaic couple is decomposed by the zinc; so that the charcoal becomes charged with  $-E$ , and the aqueous vapour and carbonic anhydride with  $+E$ .

#### CHEMICAL EFFECTS OF THE ELECTRIC CURRENT. ELECTROLYSIS.

The decomposition of chemical compounds by the electric current has been already considered in connection with the discharge of friction electricity (p. 397), and with the development of electricity by chemical action; but there are several important facts and laws relating to it which must now be more fully developed.

When an electric current passes through any compound liquid, the elements or radicles of that liquid (regarded as a binary compound) are separated and transferred in opposite directions, the one following the direction of the positive, the other that of the negative electricity, and the separation going on continuously as long as the current is kept up. The separation and transference of the elements takes place in the same manner, from whatever source the electricity may be derived; but they are exhibited most conspicuously by voltaic electricity.

This mode of decomposition is called *Electrolysis* ( $\eta\lambda\epsilon\kappa\tau\rho\omega\varsigma$  and  $\lambda\upsilon\epsilon\iota\upsilon\varsigma$ ); the compound decomposed is an *Electrolyte*; and the extremities of the metallic or other conductors by which the current enters the liquid are called *Electrodes* ( $\eta\lambda\epsilon\kappa\tau\rho\omega\varsigma$  and  $\epsilon\delta\omega\varsigma$ ). They were formerly called *poles*, but the term *electrode* is preferable, because less theoretical, a pole being usually understood as a centre of force, as in fact the metallic terminals of the voltaic battery were regarded in the earlier days of the science.\* The electrodes are in most cases surfaces of metal, but they may also be surfaces of liquid or even of air, as in the decompositions by friction-electricity described at p. 397.

Those elements or radicles which follow the direction of the current of positive electricity, and are evolved at the negative electrode, are called *electro-positive* bodies; such are for the most part hydrogen, the metals, and basic radicles in general: those which travel in the direction of the current of negative electricity and are eliminated at the positive electrode, are called *electro-negative* bodies; such are oxygen, chlorine, iodine, cyanogen, and acid radicles in general. It must be understood, however that the electric relations of elements, like the purely chemical relations of acid and base, are not absolute, but vary according to the combination in which they exist; an element which is electro-positive in one combination may be electro-negative in another.

When two platinum plates or wires connected with the poles of a voltaic battery, of not less than three pairs, are plunged into water acidulated with sulphuric acid, to increase its conducting power, streams of gas are evolved from the liquid at the surfaces of both the platinum terminals—hydrogen from that which is connected with the negative, oxygen from that which is connected with the positive, pole; and if the gases are collected in separate tubes placed over the platinum terminals, the hydrogen is found to occupy twice the volume of the oxygen. The quantity of these gases

\* The terms *electrolysis*, *electrolyte*, and *electrode* were introduced by Faraday, who further designates the surface of the electrolyte in contact with the positive electrode as the *anode*, and that which is in contact with the negative electrode as the *cathode*; he also applies the terms *anions* and *cations* to the elements evolved at the anode and cathode respectively, and includes both sets of elements under the general term, *ions*. For the derivation of these terms, see *Faraday's Experimental Researches*, series vii.; also the article *ANION* in this Dictionary.



evolved in a given time serves as a measure of the chemical power of the battery: hence an apparatus arranged for decomposing water in this manner and measuring the quantities of gas obtained is called a Voltameter. Fig. 420 represents a voltameter for

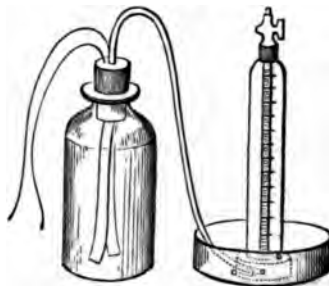
Fig. 420.



Fig. 421.



Fig. 422.



collecting the gases in separate tubes; *figs. 421, 422*, voltameters in which they are collected in the same tube: the latter is generally the more convenient form of measurement, because a larger quantity of gas is collected in a given time; but when particular accuracy is required, it is best to collect the gases separately, and measure only the hydrogen, because the oxygen is somewhat more rapidly absorbed by the water.

When hydrochloric acid is subjected to the action of the battery with platinum electrodes, hydrogen is evolved at the negative, and chlorine at the positive electrode; but with copper electrodes chloride of copper is formed at the latter. Iodide of potassium in aqueous solution, with platinum electrodes, yields iodine at the positive, and potassium at the negative electrode, the potassium not however being separated in the metallic state, but decomposing the water; so that hydrogen is evolved and a solution of potash is formed. Aqueous sulphate of sodium ( $\text{Na}_2\text{SO}_4$ ) yields in like manner sodium at the negative,  $\text{SO}_4$  at the positive electrode, the sodium being converted into soda, with elimination of hydrogen, the  $\text{SO}_4$  into sulphuric acid ( $\text{H}_2\text{SO}_4$ ) with elimination of oxygen. Aqueous sulphate of copper ( $\text{CuSO}_4$ ) yields metallic copper at the negative, and sulphuric acid at the positive electrode.

Fused iodide of lead yields iodine at the positive, lead at the negative electrode; other fused chlorides, bromides, and iodides, yield similar results.

It is only at the surface of the electrodes that any signs of decomposition are apparent; the intermediate portion of the liquid appears perfectly quiescent; nevertheless this portion forms part of the circuit along which the current passes, and must therefore be subject to its influence; indeed, if we regard the current as a succession of molecular charges and discharges, taking place throughout the circuit (p. 404), every molecule of liquid between the electrodes must experience a succession of these actions. The non-appearance of any change, except at the electrodes, is explained as follows:—

Suppose the electrolyte to be hydrochloric acid. A row of its molecules situated between the electrodes *p n* (*fig. 423*) becomes polarised by the action of the battery, the chlorine-atoms (denoted by the dark half-circles in the figure) taking a negative charge and turning towards the positive electrode, while the hydrogen-atoms (the light half-circles) take a positive charge and turn towards the negative electrode. When this state of tension has reached a certain limit, discharge takes place along the whole row of particles, the chlorine of each molecule passing on to the hydrogen of the one on its left: whence it follows that an atom of chlorine is left free at the positive, and an atom of hydrogen at the negative electrode, and the remaining atoms arrange themselves as shown in the second line of the diagram. The same process is then repeated; these molecules become polarised like those of the first row, turning their chlorine-atoms to *p*, and their hydrogen-atoms to *n*, and when the tension has reached a certain height, discharge again takes place, a second atom of chlorine being evolved at *p*, and a hydrogen atom at *n*; and in this manner the action is continued, no change

being apparent in the intermediate molecules, because one molecule of hydrochloric acid is exactly like another. The decomposition which goes on in a liquid subjected

Fig. 423.



to the action of the battery is, in fact, exactly the same as that which takes place in the cells of the battery itself, as already explained (p. 419).

A similar explanation applies to every case of the decomposition of a single electrolyte. Moreover, the same interchange of atoms may take place between two or more liquids, placed between the same electrodes and connected together by columns of liquid, as by siphon-tubes filled with water, or by moistened bundles of cotton or asbestos, as shown in *figs. 424, 425, 426*, or separated by porous diaphragms. Suppose,

Fig. 424.



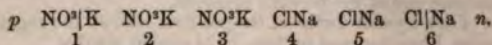
Fig. 425.



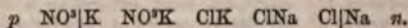
Fig. 426.



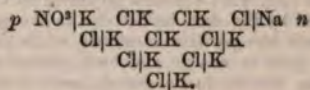
for example, the positive electrode to be immersed in a solution of nitrate of potassium, and the negative in a solution of chloride of sodium, the two liquids being separated by a partition of bladder, vegetable parchment, or porous earthenware. A series of molecules between the electrodes may be thus represented:



The atoms are then transferred in opposite directions in the manner above described, the atom  $\text{NO}^3$  in 1 being in the first instance evolved at  $p$ , and the atom of  $\text{Na}$  in 6 at  $n$ . At the same time, the  $\text{K}$  in 1 is transferred to the  $\text{NO}^3$  in 2, the  $\text{K}$  in 2 to the  $\text{NO}^3$  in 3, the  $\text{K}$  in 3 to the  $\text{Cl}$  in 4, the  $\text{Na}$  in 4 and 5 to the  $\text{Cl}$  in 5 and 6, respectively; so that the new arrangement is—



The action is then continued in the same manner, the successive steps of the decomposition being represented as follows:



In this manner, both the acid radicles are transferred to the positive and both the basic radicles (metals) to the negative electrode.

The same transference of atoms in opposite directions takes place with any number of solutions, all the acids ultimately reaching the positive, and all the bases the negative electrode, provided all the compounds formed by the several interchanges of molecules are soluble; but if an insoluble compound is formed, it falls to the bottom, is removed from the sphere of action, and its elements are not carried any further.

Thus when a solution of sulphate of potassium is placed in contact with the negative electrode, distilled water at the positive electrode, and a solution of caustic baryta between them (*fig. 425*), no sulphuric acid is transferred to the positive electrode, but a precipitate of sulphate of barium is formed in the middle liquid. Similarly with chloride of barium in the positive vessel, water in the negative, and sulphate of potassium in the middle, potash soon appears in the negative vessel, and a precipitate of sulphate of barium is formed in the middle vessel; but no baryta is transferred to the negative, or sulphuric acid to the positive electrode. When chloride of barium is placed in the negative vessel, sulphate of silver in the middle, and water in the positive vessel, thus



sulphuric acid makes its appearance after a while in the positive vessel, and a precipitate of chloride of silver is formed in the middle.

*Relation between Decomposition and Conduction.*—From the manner in which electrolytic decomposition takes place, it is manifestly dependent on that freedom of motion among the molecules of a body which is found only in the liquid state. On the other hand, the transference of atoms in opposite directions is an essential condition of the passage of electricity through compound liquids; the series of discharges between contiguous molecules, which in solid conductors takes place without permanent dislodgement of the atoms, is in the electrolyte essentially connected with the interchange of the constituent atoms. Many oxides, chlorides, and salts of various kinds, *e.g.* potash, protoxide of lead, the chlorides of the alkali- and earth-metals, sulphide of antimony, sulphide of potassium, chlorate and nitrate of potassium, borate of lead, &c. &c., which resist the passage of the voltaic current while in the solid state, conduct and suffer decomposition when fused; whereas other compounds, *e.g.* iodide of sulphur, stannic iodide, orpiment, realgar, glacial acetic acid, caffeine, spermaceti, camphor, &c., neither conduct nor are decomposed when melted. The same is true of stannic chloride, chloride of arsenic, and hydrated chloride of arsenic, which are liquid at common temperatures. (Faraday.)

There is an apparent exception to this law, with regard to water and certain other liquids, which appear to conduct feeble currents of electricity without undergoing decomposition. Thus Faraday found that when acidulated water, solution of sulphate of sodium, fused nitre, fused chloride of lead, fused chloride of silver, or fused iodide of lead, was placed, together with solution of iodide of potassium, in the circuit of a single pair of zinc and platinum plates excited by dilute acid, the iodide of potassium was decomposed, but not the other electrolyte, which therefore appeared to conduct without decomposing. According to Jacobi also, the current of a single pair does not decompose water, and yet produces deflection of the galvanometer. If the current of a ten-pair battery be weakened, by the interposition of a long thin wire, to such a degree, that it produces the same deflection of the galvanometer needle as the current of a single pair, it likewise appears to pass through water without producing decomposition.

This passage of feeble currents through electrolytes without decomposing them, appears at first sight to be at variance with the law of definite electrolytic action (*p. 438*). The anomaly, however, is only apparent. It is true that no gas is obtained when a feeble current is passed into acidulated water by means of platinum plates; nevertheless the water is decomposed, but so slowly that the oxygen and hydrogen gases liberated on so large a surface, partly surround it as an envelope, and are partly absorbed by the water. The decomposition may, however, be made apparent by placing the apparatus under an exhausted receiver, the gases then making their appearance on the surface of the plates. Another mode of rendering decomposition by feeble currents visible is to reduce the surface of one of the electrodes. Thus, if one of the electrodes consists of a platinum plate and the other of a fine platinum wire covered with glass up to its very point, gas is evolved from the surface of this wire, partly because there is no surface to which it can attach itself, and partly perhaps because the large surface of the other electrode intensifies the polarisation of the metal point, and of the particles of electrolyte in contact with it, just as a metal plate or the extended hand does, when held before a pointed rod inserted into the conductor of an electrical machine (*p. 389*). The evolution of gas from the wire ceases, however, after a short time, but may be renewed by increasing the surface of the other electrode, or by reversing the current, which destroys the polarisation of the electrodes (*p. 429*).

**Secondary products of Electrolysis.** It is but rarely that both elements of an electrolyte are separated at the electrodes in the free state, one or both of them frequently entering into some new combination, either with substances contained in the solution,



or with the electrodes themselves. Instances of this secondary action have been already noticed in speaking of the electrolysis of sulphate of sodium and other salts, and many others may be given. In a mixture of hydrochloric and hydriodic acids nothing but iodine would be evolved at the positive electrode, because, though both acids might be decomposed at once by the current, the chlorine, as soon as liberated, would decompose another portion of the hydriodic acid, combining with the hydrogen and liberating an equivalent quantity of iodine.

When an aqueous solution of acetate or nitrate of lead is electrolysed, metallic lead is deposited on the negative, and peroxide of lead on the positive electrode, the latter being formed by the action of oxygen separated from the water on the lead in the solution; accordingly the quantity of oxygen gas evolved at the positive electrode is considerably less than in a voltameter included in the same circuit.

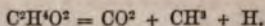
Aqueous ammonia yields, by electrolysis with platinum electrodes, pure nitrogen at the positive and hydrogen at the negative electrode, the volume of the latter being three or four times greater than that of the former. The gases are not, however, evolved by the direct action of the current; for the proportion of nitrogen is not constant, but varies with the strength of the solution, whereas the volume of hydrogen evolved is exactly equal to that in a voltameter included in the same circuit: whence it appears that the water of the aqueous ammonia is decomposed by the current, and the nitrogen evolved at the positive electrode results from the decomposition of the ammonia by nascent oxygen, with which indeed it is often mixed to a small amount.

Nitric acid yields oxygen at the positive electrode, in quantity equal to that in a voltameter in the same circuit; no gas is evolved at the negative electrode, but the nitric acid is there reduced to nitrous acid and nitric oxide, which colour the liquid yellow or red. This result is due, partly to the electrolysis of the water, the hydrogen from which reduces the nitric acid at the negative electrode, partly to the direct decomposition of the nitric acid itself, into  $\text{NO}^2$  and  $\text{H}$ , the  $\text{NO}^2$  being transferred to the positive electrode, where it decomposes water, reproducing nitric acid and eliminating oxygen. In consequence of this action, the strength of the acid increases around the positive electrode.

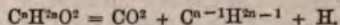
The substances eliminated from a solution by the action of the current sometimes enter into combination with the electrodes. This is especially the case when the positive electrode is formed of an oxidable metal; thus, when acidulated water is decomposed with a plate of copper or iron for the positive electrode, no oxygen is evolved, but the metal dissolves in the acid. On the other hand, when the negative electrode is coated with a metallic oxide, especially with a peroxide (such as  $\text{MnO}$  or  $\text{PbO}$ ), the hydrogen reduces this oxide and forms water. Actions of this kind taking place at the electrodes greatly assist the decomposition, by inducing a polarisation of the molecules of the electrolyte in the same direction as that induced by the action of the battery.

Becquerel (*Traité de l'Electricité et du Magnétisme*, 1835, tom. iii. pp. 294—330), by exposing different solutions to the action of feeble electric currents with electrodes of various nature, has obtained many metallic compounds, viz. oxides, sulphides, iodides, &c., and even the sulphate and carbonate of barium, in regular crystals.

Organic compounds subjected to electrolysis yield numerous secondary products. A solution of acetate of potassium divided into two parts by a porous diaphragm, to prevent the mixing of the gases evolved at the two electrodes, yields pure hydrogen, together with potash, at the negative electrode, and at the positive (if of platinum) a mixture of carbonic anhydride and methyl-gas, with a small quantity of oxide of methyl:



We may suppose that the acetic acid is resolved by the current into  $\text{H}$  and  $\text{C}^2\text{H}^3\text{O}^2$ , the latter then splitting up into  $\text{CO}^2$  and  $\text{CH}^3$ . Other acids of the adipic series,  $\text{C}^n\text{H}^{2n}\text{O}^2$ , are decomposed in a similar manner, the general formula of the decomposition being



An aqueous solution of ethylsulphate of potassium yields, at the negative electrode potash and hydrogen, and at the positive, ethylsulphuric acid, which, if the positive electrode is formed of amalgamated zinc, forms ethylsulphate of zinc, but if the positive electrode is of platinum, is resolved, partly by oxidation, into carbonic anhydride, aldehyde, and sulphuric acid. Amylsulphate of potassium with platinum electrodes yields potash and hydrogen at the negative electrode, and at the positive, free sulphuric acid and oxygen, with an odour of valeric acid. Amylphosphate of potassium

yields in like manner, at the positive electrode, oxygen, carbonic acid, and phosphoric acid, with an odour of valeric or butyric acid. (Guthrie, Chem. Soc. Qu. J. ix. 131.)

**Electrolytic reduction of Metals.** All metals may be reduced by electrolysis from one or other of their compounds, either in the fused state or in aqueous solution. Several examples of these reductions have already been mentioned. The less oxidable metals, such as copper, lead, tin, and other noble metals, are reduced from the solutions of their salts with the utmost ease, even by the current of a single pair. Indeed, as explained at page 420, every precipitation of one metal by another, such as that of copper by iron, lead and tin by zinc, silver by copper, &c., is an example of electrolytic decomposition. The electrotype process and the processes of electro-silvering and electro-gilding also belong to the same order of phenomena. For the details of these processes we must refer to *Ure's Dictionary of Arts, Manufactures, and Mines*, article **ELECTRO-METALLURGY**.

The electrolytic process is also used for the detection of metals in toxicological investigations, &c. It has long been applied to the detection of small quantities of mercury, a thin plate of gold being used as the negative electrode, so that the mercury may form an amalgam with it. In 1850, Gaultier de Claubry (J. Pharm. [3] xvii. 125; Chem. Soc. J. ii. 167) proposed its application to the detection of other metals, e.g. arsenic, antimony, lead, copper, zinc, &c., and more recently Bloxam (*ibid.* xiii. 14) has applied it to the detection of arsenic, a solution of arsenious acid acidulated with sulphuric or hydrochloric acid and decomposed by the electric current, giving off the greater part of its arsenic as arsenetted hydrogen (i. 362).

The reduction of the more oxidable metals requires, for the most part, more powerful currents and peculiar arrangements, to prevent the recombination of the metal with the oxygen, chlorine, or other element, from which it has been separated, and at the same time to concentrate the force of the current at the point of reduction. The latter object may be effected by reducing the negative electrode to a fine point, and giving the positive electrode a considerable surface, as already described with reference to the decomposition of water by feeble currents. Bunsen finds that, with a given battery power, the reducing force of the current varies nearly in the inverse ratio of the transverse section of the electrode at which the reduction takes place. Thus, a current of constant strength passed through an aqueous solution of sesquichloride of chromium, eliminates, as the cross section of the negative electrode is diminished, hydrogen, chromic oxide, chromous oxide, and finally metallic chromium. (Pogg. Ann. xci. 619.)

It was by an arrangement based on this principle, and with the aid of a powerful battery, that Davy succeeded in isolating the metallic bases of the alkalis. Thus, to reduce *potassium*, hydrate of potassium contained in a platinum capsule was moistened with a small quantity of water, and brought in contact with the end of a platinum wire connected with the negative pole of a powerful voltaic battery, the positive pole of which was connected with the capsule. Potassium then collected round the wire in small metallic globules, most of which, however, took fire in the air, and were reconverted into caustic potash. By making a hole in the lump of hydrate of potassium, filling it with mercury, and dipping the negative wire into the mercury, the reduction is much more easily effected, the potassium forming an amalgam, from which the mercury may afterwards be removed by distillation. The reduction of *sodium* is effected by similar methods.

*Barium* may be obtained by subjecting the chloride mixed up to a paste with water and a little hydrochloric acid, at the temperature of 100° C., to the action of the electric current, using for the negative electrode an amalgamated platinum wire. A crystalline amalgam is thus obtained, from which the mercury may be distilled off in a stream of hydrogen. *Strontium* may be obtained in a similar manner; also *calcium*, though less easily, because the point of the wire becomes covered with a crust of lime, which interrupts the current. (Bunsen, Pogg. Ann. xci. 619.)

Some of the alkali- and alkaline-earth-metals form fusible chlorides, from which the metals are easily obtained by electrolysis.

*Lithium* may be reduced by subjecting its chloride, fused over a spirit-lamp in a small porcelain crucible, to the action of a Bunsen's battery of four to six cells. The positive electrode is formed of a small splinter of gas-coke, and the negative of an iron wire, about as thick as a knitting-needle. After a few seconds, a small, silver-white regulus is formed round the wire, under the fused chloride. It may be lifted out of the fused mass, together with the wire electrode, by means of a small flat iron spatula, the wire withdrawn with the still melted metal, which is protected from oxidation by a coating of chloride of lithium, and the metal removed from the spatula by a pen-knife, after having been cooled under rock-oil. These operations may be repeated every two or three minutes, and thus an ounce of the chloride reduced in a very short time. (Bunsen, *loc. cit.*)

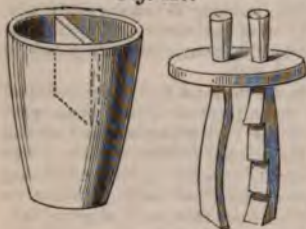


*Strontium* is likewise obtained from the fused chloride. A small porcelain crucible, having a porous cell in the middle, is filled with anhydrous chloride of strontium, mixed with a little sal-ammoniac, the level of the salt within the cell being considerably higher than in the crucible. The negative electrode, which is placed within the porous cell, consists of a very thin iron wire, wound round a thicker one, and then covered with a piece of tobacco-pipe stem, so that only  $\frac{1}{8}$  of an inch of it appears below; the positive electrode is an iron cylinder, placed in the crucible round the porous cell. The heat is regulated during the experiment, so that a crust may form in the cell. The metal then collects under this crust, without coming in contact with the sides of the crucible. By this method, pieces of the metal weighing half a gramme are sometimes obtained. (Matthiessen, Chem. Soc. Qu. J. viii. 107.)

*Barium* may be reduced, in like manner, from the chloride, but only as a metallic powder; and *calcium* from a mixture of 2 at. chloride of calcium, 1 at. chloride of strontium, and a little sal-ammoniac. (Matthiessen.)

*Magnesium* is separated from the fused chloride as follows:—A porcelain crucible (fig. 427) is divided in half in its upper part by a vertical diaphragm (made out of a

Fig. 427.



thin porcelain crucible-cover, and fitted with a lid filed from a tile), through which the extremities of the electrodes, made of gas-coke or Bunsen's charcoal (i. 760), are introduced into the two halves of the crucible. The crucible is then heated to redness, together with the cover and the electrodes, filled with fused chloride of magnesium, and subjected to the action of a 10-pair Bunsen's battery. The negative electrode is cut like a saw, so that the magnesium, as it separates, may lodge in the cavities, and not float on the surface of the specifically heavier liquid. (Bunsen, Ann. Ch. Pharm. lxxxii. 137.) According to Matthiessen (Chem. Soc. Qu. J. viii. 107), the metal may be much

more easily obtained from a fused mixture of 4 at. chloride of magnesium and 3 at. chloride of potassium, with a little sal-ammoniac; the cutting of the negative electrode may then be dispensed with, as the metal is heavier than the fused salt. A simple mode of effecting the reduction is to fuse the mixture in a common clay tobacco-pipe over a lamp, the negative electrode being formed of an iron wire passed up the pipe-stem, and the positive of a piece of gas-coke, just touching the surface of the fused chlorides. (Matthiessen.)

*Aluminium* may be obtained by similar methods from the fused chloride of aluminium and sodium. But as this salt fuses at a very moderate heat, at which the aluminium does not fuse, but separates as a powder, pulverised chloride of sodium should be gradually added during the reduction, in sufficient quantity to raise the temperature nearly to the melting point of silver. The aluminium then separates in large metallic globules. (Bunsen; Deville.)

For the reduction of certain metals from solutions, Bunsen arranges the decomposing cell as follows:—The positive electrode is formed of the inner concave surface of a charcoal crucible, filled with hydrochloric acid and standing within a porcelain crucible. The liquid to be decomposed is contained in a small porous cell standing in the carbon crucible, and the negative electrode is formed of a wire or narrow strip of platinum dipping into the liquid. The whole is heated over the water-bath. A concentrated solution of chromic or manganous chloride, subjected in this manner to the action of a 4-pair Bunsen's battery, quickly yields large lumps of the metal chemically pure.

#### *Law of Definite Electrolytic Action.*

Faraday first demonstrated the important law that: *The quantity of any electrolyte decomposed by the electric current is constant for a given quantity of electricity.* Suppose a number of voltmeters with platinum electrodes (p. 433) to be traversed by the same electric current, not divided between them, but passing through them all in succession; then it is found that the quantities of oxygen and hydrogen gases collected in a given time, are the same in all the voltmeters, even though the water contained in them may be acidulated in different degrees, and the electrodes may be of different sizes. The quantity of electricity which passes is determined by the resistance of the liquid which possesses least conducting power, and this quantity of electricity decomposes the same amount of water in all parts of the circuit. As, however both the gases are slightly soluble in water, and the oxygen more so than



the hydrogen, it is necessary to guard against errors thence arising, by placing the electrodes very close to one another, and at equal distances in all the voltmeters, so that the gases may have only a short column of liquid to traverse, and not to leave the gases long in contact with the liquid, especially if the electrodes have large surfaces. As oxygen is more soluble in water than hydrogen, more exact results are obtained by collecting the hydrogen alone than the two gases together.

If the same current be divided between two voltmeters (by means of a branching conductor), and then made to pass wholly through a third voltmeter, the quantities of hydrogen evolved in the first two are together equal to that evolved in the third; and if the current is equally divided between the first two (as measured by the galvanometer) the quantities of hydrogen collected in them are equal to one another.

*When the same current passes successively through different electrolytes, the quantities of these compounds decomposed and of the several elements eliminated, are chemically equivalent to each other.*

Faraday decomposed fused stannous chloride ( $\text{SnCl}_2$ ) by a current which also traversed a voltmeter containing acidulated water. Into the chloride contained in a bent glass tube, and kept in a state of fusion by a spirit-lamp, two platinum wires were inserted, one connected with the negative pole of a voltaic battery, the other with one of the electrodes of the voltmeter, the second electrode of which was connected with the positive pole of the battery. Tin was then deposited on the negative electrode in the fused chloride, and at the same time the water in the voltmeter was decomposed.

The experiment having been continued till the quantity of mixed oxygen and hydrogen gases collected in the voltmeter amounted to 3.85 cubic inches, or 0.497 grains, the metallic tin deposited in the same time was found to weigh 3.2 grains. Now, these two quantities are very nearly in the ratio of the atomic weights of water and tin: for  $0.497 : 3.2 = 18 : 115.8$ . The difference between the number thus obtained and 118, the true atomic weight of tin, probably arose from the action of the chlorine evolved at the positive electrode on the tin, whereby a certain quantity of chloride was reproduced, the arrangement adopted not being capable of effecting a very complete separation. Four experiments made in a similar manner gave for the atomic weight of tin, as determined by electrolysis, the number 117.16.

The decomposition of chloride of lead in a similar manner, the positive electrode being formed of plumbago, gave for lead the number 100.85, the true atomic weight being 103.6. An experiment with borate of lead gave 101.29.

Faraday, in his "Experimental Researches" (ser. vii.), supposes that it is only compounds which, according to the atomic weights at that time generally adopted, are composed of 1 at. of each of their components, *e.g.* water =  $\text{HO}$ , hydrochloric acid  $\text{HCl}$ , sulphate of copper,  $\text{CuSO}_4$ , &c., that can be decomposed by the electric current. Subsequent experiments by Matteucci and E. Becquerel have shown, however, that this is not the case; for trichloride of antimony, and cuprous as well as cupric chloride, also several basic nitrates and nitrites of lead, and other salts of various composition, must be ranged among electrolytes. E. Becquerel finds that when trichloride of antimony is electrolysed in the same circuit with a voltmeter, for each atom of hydrogen evolved in the latter, 1 at. chlorine and  $\frac{1}{3}$  at. antimony are separated (or for 3 at. hydrogen 3 at. chlorine and 1 at. antimony). With sesquichloride of iron,  $\text{Fe}^{\text{III}}\text{Cl}_3$ , 1 at. chlorine and  $\frac{2}{3}$  at. iron are separated for each atom of hydrogen in the voltmeter. Cuprous chloride,  $\text{Cu}^{\text{I}}\text{Cl}$ , gives 1 at. chlorine and 2 at. copper for 1 at. hydrogen.

The general result may be thus stated:—*The quantities of any number of electrolytes decomposed by the same electric current passing through them in succession, are such as contain equal numbers of atoms of hydrogen, or equivalent quantities of any other radicles, positive or negative.* Thus the quantities of the several electrolytes in the following table, which would be decomposed by the same current, are such as are expressed symbolically in the second column, and by their equivalent weights in the third.

	Formula.	Equivalent Weight.
Water . . . . .	$\text{H}^{\text{O}}$	18
Hydrochloric acid . . . . .	$\text{H}^{\text{I}}\text{Cl}^{\text{I}}$	73
Cupric chloride . . . . .	$\text{Cu}^{\text{II}}\text{Cl}_2$	134.2
Cuprous chloride . . . . .	$\text{Cu}^{\text{I}}\text{Cl}_2$	217.4
Stannous chloride . . . . .	$\text{Sn}^{\text{II}}\text{Cl}_2$	189
Antimonious chloride . . . . .	$\frac{2}{3}(\text{Sb}^{\text{III}}\text{Cl}_3)$	152.3
Ferric chloride . . . . .	$\frac{2}{3}(\text{Fe}^{\text{III}}\text{Cl}_3)$	108.3
Sulphuric acid . . . . .	$\text{H}^{\text{I}}\text{SO}_4^{\text{I}}$	98
Cupric sulphate . . . . .	$\text{Cu}^{\text{II}}\text{SO}_4$	169.2

When an aqueous solution, or a mixture of different electrolytes, is subjected to the action of the current, secondary actions intervene, leading to results which, at first sight, appear inconsistent with the law of definite electrolytic action. Thus, when a solution of sulphate of sodium is electrolysed, sulphuric acid and free oxygen are eliminated at the positive electrode, soda and hydrogen at the negative; and Daniell has shown that, if a voltmeter containing acidulated water is interposed in the same circuit, the quantities of oxygen and hydrogen evolved from the saline solution are equal to those evolved from the water in the voltmeter; and at the same time, if the saline solution is strong, quantities of sulphuric acid and soda exactly equivalent to these quantities of oxygen and hydrogen are separated from the salt. Here, then, the same current appears to do twice as much chemical work in the solution of sodic sulphate as in the voltmeter. This anomaly is, however, only apparent; the fact being that, in a solution of a certain strength, only the sodic sulphate,  $\text{Na}_2\text{SO}_4$ , is directly decomposed by the current, the sodium going to the negative, the oxysulphone ( $\text{SO}^4$ ) to the positive electrode. Neither of these radicles is, however, eliminated in the free state: for the sodium decomposes the water near the negative electrode, forming soda and eliminating hydrogen; and the oxysulphone decomposes the water near the positive electrode, forming sulphuric acid,  $\text{H}_2\text{SO}_4$ , and eliminating oxygen; and as the quantities of sodium and oxysulphone directly eliminated by the current are equivalent to the hydrogen and oxygen evolved in the voltmeter ( $\text{Na}^2$  and  $\text{SO}^4$  in the one,  $\text{H}^2$  and  $\text{O}$  in the other), it follows—1. That the quantities of hydrogen and oxygen evolved from the saline solution are equal to those evolved in the voltmeter.—2. That equivalent quantities of sulphuric acid and soda are afterwards found at the two electrodes.

If the solution contains a salt of any metal not capable of decomposing water, such as sulphate of copper, the metal is deposited on the negative electrode, in quantity equivalent to the hydrogen evolved in the voltmeter, and no hydrogen is separated at the negative electrode; while at the positive electrode sulphuric acid is formed, and oxygen evolved as above. In dilute solutions, the water and the salt are decomposed simultaneously by the current, in quantities which are together equivalent to the quantity of water decomposed in the voltmeter. Thus, suppose that a dilute solution of sulphate of copper yields 2 grains of hydrogen, while 3 grains of that gas are collected in the voltmeter; then the quantity of copper reduced at the negative electrode will be the equivalent of the remaining 1 grain of hydrogen in the voltmeter, that is to say, 31.6 grains.

When water acidulated with sulphuric acid is decomposed by the current, the sulphuric acid,  $\text{H}_2\text{SO}_4$ , is decomposed as well as the water—the  $\text{SO}^4$  going to the positive electrode, where it eliminates oxygen and forms sulphuric acid: consequently, that acid accumulates about the positive electrode. The quantities of hydrogen and oxygen evolved are clearly the same as if the water alone were decomposed.

In the electrolysis of dilute hydrochloric acid, both the acid and the water are decomposed—the chlorine and oxygen evolved at the positive electrode being together equivalent to the hydrogen set free at the negative electrode.

An aqueous solution of peroxide of hydrogen ( $\text{H}_2\text{O}_2$ ) yields, by electrolysis, a quantity of hydrogen equal to that evolved from water in the same circuit, and consequently a double quantity of oxygen. This apparent anomaly may be explained by regarding peroxide of hydrogen as a compound of water and oxygen; and supposing that the water is resolved by the current into  $\text{H}^2$  and  $\text{O}$ , its decomposition necessarily involving the elimination of the second atom of oxygen which had been united with it.

In all cases of mixtures of two or more electrolytes, the sum of the quantities decomposed is the equivalent of the quantity of any one of them that would be decomposed by the same current acting for the same time—or, which comes to the same thing, of the quantity of water simultaneously decomposed in a voltmeter. The proportion of each compound decomposed depends upon the nature of the electrolytes, and the proportions in which they are mixed. In concentrated aqueous solutions of the chlorides, bromides, and iodides of hydrogen and the metals, it is only these compounds that are directly decomposed by the current; but in dilute solutions, the water is decomposed at the same time.

#### *Relations between the Quantity and Intensity of the Current and its Decomposing Power.*

The chemical action which takes place in the cells of the battery is likewise equivalent to that which is produced in the decomposing cells, provided there is no local action (p. 418) on the surface of the positive metal. If a battery could be so constructed that there should be no local action, this relation would be strictly true; that is to say, in a battery composed of amalgamated zinc, dilute sulphuric acid, and

platinum, the volume of hydrogen evolved from the surface of each platinum plate would be equal to that evolved in a voltmeter placed in the same circuit, and the quantity of zinc dissolved in each cell would be the exact equivalent of this, viz. 32.5 pts. of zinc dissolved in each battery-cell for every 1 pt. of hydrogen evolved in the voltmeter. As, however, it is impossible to prevent local action altogether, the quantity of zinc dissolved in each cell is always somewhat greater than this proportion would indicate; thus Jacobi found that in a Daniell's battery with amalgamated zinc plates, 33.6 pts. of zinc were dissolved in each cell for every 9 pts. of water decomposed in the voltmeter.

Hence it follows that, with a given intensity of chemical action in the battery-cells, and a given conducting power throughout the circuit, the amount of electrical or chemical power developed by the battery, as measured by the voltmeter, is proportional to the surface of each plate exposed to the action of the liquid, in other words, to the area of the transverse section of that liquid, supposing the action in all the cells to be uniform. If, however, the chemical action in any one of the cells should be weaker than in the rest, then that cell presents, to a certain extent, an obstacle to the passage of the electricity developed by the rest, and the whole force of the battery is lowered; or, again, if the conducting power of the circuit is lessened by the interposition of a long wire, or of another decomposing cell, or of an electrolyte more difficult of decomposition, the quantity of electricity which can pass through the circuit in a given time, and therefore also the amount of chemical work which the battery is capable of performing in that time, is also lessened, and cannot be increased by augmenting the size of the plates, without, at the same time, increasing their number, which, as already explained, determines the intensity of the current, that is to say, its power of overcoming resistance. If, however, by increasing the number of pairs, or otherwise, the tension has been raised to such a degree that all the electricity evolved from the source in a given time is able to enter the liquid—so that the galvanometer shows the same deflection whether the circuit be closed by a metallic conductor or by a liquid—a further rise of intensity does not accelerate the decomposition.

The following experiments were made by Matteucci to determine the proportion in which the decomposition of different liquids, and therefore also the quantity of the current, increases with the number of pairs.

In A, a pile was constructed of zinc and copper with solution of sal-ammoniac; in B, with water containing nitro-sulphuric acid; and in C with spring-water; in D a battery of zinc and platinum in dilute sulphuric acid was employed. The liquid in the decomposing cell was water = Aq., or a solution of 1, 4, 8, or 10 pts. of sal-ammoniac in 100 pts of water = Sm 1, Sm 4, Sm 8, Sm 10; or saturated solution of sal-ammoniac = Sm s; or dilute sulphuric acid = Sf; or a solution of 1 pt. of sulphate of zinc (zinc-vitriol) in 100 pts. of water = ZV; or solution of iodide of potassium = IK. PZ denotes the number of pairs employed. The degrees under A, B, C give the deflection of the galvanometer; the numbers under D denote the relative quantity of hydrogen gas evolved from the solution of iodide of potassium.

A.						B.			
PZ.	Aq.	Sm 1.	Sm 4.	Sm 10.	Sf.	Aq.	Sm 1.	Sm 8.	Sm s.
	1°	6°	8°	9°	10°	1°	7°	15°	38°
1	1	12	17	21	27	2	14	34	60
2	1	15	19	26	27	3	22	40	
3	3	16	22	27	27	6	25	60	
4	3	18	27	27	27	6	33	74	

C.					D.	
PZ.	Aq.	Sm s.	ZV.		PZ.	IK.
10	1	14°	2°		1	1
20	1	17	3		2	8
30	2	18	7		3	17.5
40	2	15	8		4	65
50	3	12	7			
60	3	11	7			

In the following experiments of Jacobi and Walker, Daniell's constant battery was used. The quantity of detonating gas developed in the decomposing cell in a given time, according as a greater or lesser number of plates were connected together, was determined in measures. In Jacobi's experiments, and in those of Walker, given under *a* and *b*, the decomposing cell contained water acidulated with sulphuric acid; in *c* it contained distilled water.



Jacobi.				Walker.			
PZ.		PZ.		PZ.	a.	b.	c.
2	1	8	54	20	1	— 1	—
3	12	9	59	40	1.2	— 1.06	— 1
4	22	10	67	60	1.3	— 1.06	— 1.57
5	33	11	68	80	1.4	— 1.12	— 2.13
6	42	12	75	100	1.5	— 1.12	— 3.47
7	49	13	80	120	1.55	— 1.12	— 3.88
				140	1.5	— 1.16	— 6.60
				160	1.5	— 1.19	— 8.25

The more readily the atoms of a liquid are transposed—whether from its peculiar nature or from the thinness of the film of liquid between the electrodes,—the smaller is the tension which the electric current requires in order to penetrate it, the greater the quantity of electricity which flows into the liquid from a given source, and the greater the quantity of liquid decomposed in a given time.

Aqueous solution of iodide of potassium may be decomposed by a current of the smallest tension; next in order of facility come fused chloride of silver, fused protochloride of tin, fused chloride of lead, fused iodide of lead, water containing hydrochloric acid, water containing sulphuric acid. That the chloride of lead is more easily decomposed than the iodide, perhaps arises from the platinum electrode having a greater affinity for chlorine than for iodine. (Faraday, see page 417.)

Thermo-electric currents, weak both in quantity and intensity, decompose nitrate of silver, when the electrodes consist of platinum, but not salts of copper, lead, tin, or zinc; in these also electrodes of gold or silver produce no effect. But when the electrodes consist of the same metal as that in the solution, decomposition is easily effected, *e.g.* nitrate of silver with silver electrodes, sulphate of copper with copper, stannous chloride with tin, acetate of lead with leaden electrodes. Platinum wires produce no effect in solutions of platinum. A thermo-electric current is best conducted into a solution of common salt by means of wires of zinc, tin, lead, or iron—less readily by copper, with difficulty by silver, and not at all by platinum.

The current of the electrical machine, which is of very high intensity, is capable of passing through any electrolyte whatever; but the amount of decomposition which it produces is extremely small compared with that of the smallest voltaic apparatus (see p. 397): hence we may conclude that the quantity of electricity developed by the electrical machine, or any other friction apparatus, is very small as compared with that developed by chemical action.

#### MAGNETIC ACTION OF THE ELECTRIC CURRENT—ELECTRO-MAGNETISM.

A magnetic needle, balanced on its centre and placed in the neighbourhood of a wire, or other conductor, along which a current of electricity is passing, tends to place itself at right angles to the line of the current. This effect, which we have already had frequent occasion to notice, is produced by the electric current, from whatever source it may be derived; but it depends on the quantity of electricity in the current, not on its intensity, and is therefore exhibited by voltaic, and even by thermo-electric currents, in a much higher degree than by those resulting from friction electricity (p. 399). Very small wires of zinc and copper excited by dilute acid will produce a stronger deflection of the magnet than the most powerful electrical machine. The deflection of the magnet is exclusively an effect of electricity in the state of motion or discharge; the highest charges, either of the voltaic battery or of the electrical machine in the state of tension, have no effect whatever on the magnet.

The direction assumed by a magnetic needle under the influence of the current may be determined by either of the following empirical rules:—

1. *Let the observer fancy himself extended in the direction of the current, looking towards the needle, and with the current of positive electricity flowing from his head to his feet: then the north pole of the needle will move towards his right hand.*

2. *The north pole of the needle tends to revolve round the conducting wire in the direction of the hands of a watch, the face of which is turned towards that end of the wire from which the positive electricity proceeds.*

Either of these rules will determine the direction taken by the needle in any case whatever; the second is perhaps the more convenient of the two. As a particular example, we may mention, that if the conducting wire is horizontal, and in the direction of the magnetic meridian, the current of  $+E$  running from north to south, the needle turns its north pole to the west if placed above the wire, and to the east if placed below.

When the magnet is freely suspended by its centre, it tends to place itself at right angles to the current, its actual position of equilibrium being intermediate between this and the direction imparted to it by the earth's magnetism; *e. g.* if placed above a horizontal conducting wire in the magnetic meridian, with the current running from south to north, the north pole points in a direction between north and east, inclining to the one or the other, according as the earth's magnetism or the current acts more strongly upon it.

As the direction of the needle under the influence of the current is reversed, either by reversing the direction of the current itself, or by moving the needle to the opposite side of the wire—*e. g.* below if it was previously above—it follows that, if the conducting wire be bent back upon itself, and the needle placed between the two arms, as in *fig. 428*,\* the two portions of the current above and below the needle will tend to give it the same direction, so that the force with which the current acts upon it will be doubled; it is even more than doubled, because the vertical parts of the wire likewise tend to turn the needle in the same direction, as may be easily seen by the rules

Fig. 428.

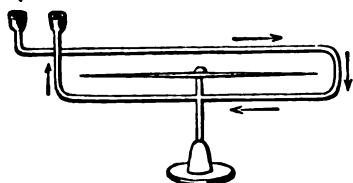
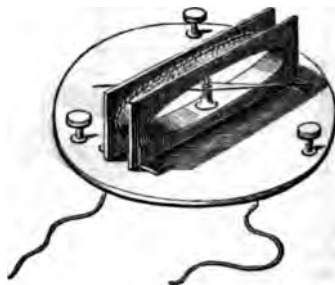


Fig. 429.



above given (p. 442). Hence also, if the needle is placed in the centre of a circular or of a square conductor (*fig. 429*) round which the current is passing, it will be moved in one direction by the joint action of all parts of this conductor. Further, if the wire be coiled several times upon itself always in the same direction, and a current sent through it from end to end, a needle placed in the centre of the coil, as in *fig. 429*, will be deflected in one direction by the joint action of all parts of the coil.

An instrument thus constructed is called a *galvanometer* or *multiplier*; it serves to indicate the existence of very feeble currents, and by the magnitude of the angle through which the needle is deflected by different currents, an approximate indication of their relative strength may be obtained. The angle of deflection is not, however, exactly proportionate to the strength of the current, so that the instrument constructed as above is not properly speaking a galvanometer, but only a *galvanoscope*; the former term is, however, in common use. Galvanometers constructed for exact measurement will be described hereafter.

The delicacy of the instrument is greatly increased by making use of an *astatic needle*—that is to say, of a magnetic needle so mounted that the action of the earth's magnetism upon it is neutralised. This is effected by joining two magnetic needles of equal powers, parallel to each other, but with their poles in contrary directions, by a small piece of straw or copper wire passing through their centres of gravity. One of these needles is placed within the coil, and the other above, in which position it is easy to see that they will both be deflected by the current in the same direction: if their similar poles pointed the same way, the upper part of the coil would turn them in opposite directions, inasmuch as one of them is above and the other below it.

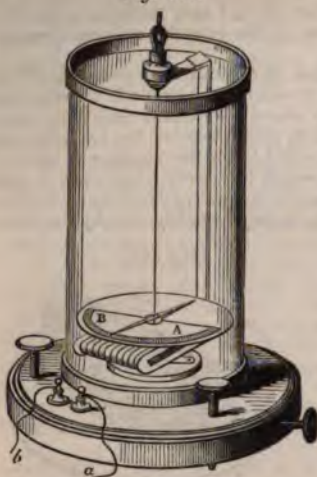
With a given length of coil, the instrument is more delicate in proportion as the magnetic power of the two needles is more nearly equal; if exactly equal, they will place themselves at right angles to the coil under the influence of the feeblest current; but it is generally desirable to leave a certain difference between them, in order that the amount of deflection may give some idea of the comparative strength of the current.

*Fig. 430* represents a galvanometer fitted up with an astatic needle, moving over a graduated arc. The needle is suspended by a thread of unspun silk, and the whole is covered with a glass case to protect the needle from the agitation of the air. The

\* The arrows in the figure indicate the direction of the current of + E; and in all that follows, the expression "direction of the current" is to be understood as applying to the positive current.

wire is coiled round a wooden frame, and is covered with silk to insulate the several turns of the coil, so that the current may not pass from one to the other, instead of going through the entire length of the wire.

Fig. 430.



The length and thickness of the galvanometer wire vary according to the kind of current which the instrument is intended to indicate. For voltaic currents, a wire about  $\frac{1}{4}$  millimetre in diameter, and making about 800 turns round the frame, is generally well adapted. Thermo-electric currents, which are of very low intensity, require a much thicker and shorter wire, *e.g.*  $\frac{3}{4}$  millimetre in diameter, and coiled thirty times round the frame. On the other hand, currents small in quantity, but of high intensity, are best indicated by a coil of very fine wire, making from 1,000 to 2,000 turns.

The insulation of the several turns of the coil, one from the other, is of very great importance, especially for currents of high intensity, such as those from the electrical machine (p. 399). M. Colladon of Geneva, who first observed the deflection of the needle by the machine current, used a galvanometer of 500 to 1,000 turns, having a wire twice covered with silk, and each series of turns separated from that below it by a sheet of oiled silk.

The direction of the current which deflects the galvanometer needle in a particular way is easily determined by the rules given on p. 442, when the direction in which the wire is coiled round the frame is known. For this purpose it is necessary to distinguish between right-handed and left-handed coils or helices. Suppose the wire to be coiled round a cylinder beginning at the left hand; then if the turns in front of the cylinder proceed from below upwards, as in *fig. 431*, the coil is left-handed; if, on

Fig. 431.

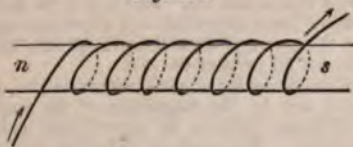
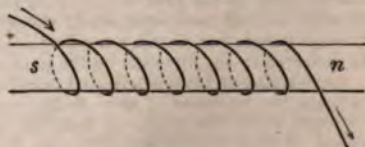


Fig. 432.



the contrary, they proceed in front from above downwards, as in *fig. 432*, it is right-handed.

A magnetic needle placed with its centre in the axis of such a coil, turns its north or south pole towards that end of the coil at which the current enters, according as the coil is left or right-handed.

The direction given to the needle is the same, whether the coil is elongated, as in *figs. 431, 432*, or compressed, as in the galvanometer. As, however, in the galvanometer when complete, it is not easy to see whether the coil is right or left-handed, it is best to determine by experiment, once for all, the direction taken by the needle when the current enters at one particular end of the coil.

#### *Action of the Magnet on the Electric Current.*

The action between the current and the magnet is mutual, so that if the conductor conveying the current is free to move, it is deflected in the direction opposite to that which the magnet takes under its influence: in short, if the magnet and conducting wire are both free to move, they place themselves at right angles to each other, the magnet moving in the manner pointed out at p. 442, the conductor in the contrary direction.

The action of the magnet on the current may be shown by means of Ampère's apparatus (*fig. 433*). On holding a bar-magnet below the rectangular wire and parallel to its lower horizontal arm, the wire turns round and places itself at right angles to the magnet, the position of equilibrium being determined by the rules given on p. 442.



Fig. 433.

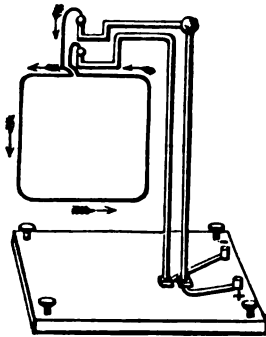


Fig. 434.



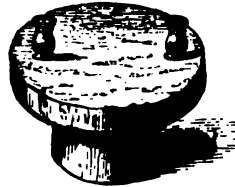
A simpler apparatus for the same purpose is the *floating battery* (fig. 434) contrived by G. De la Rive. It consists of a pair of zinc and copper plates attached to a cork, and connected together by a coil of covered wire placed above the cork; the whole is floated on water slightly acidulated, whereby a current is made to pass round the coil. On the approach of a magnet, the coil takes up a position indicated by the law just cited.

The action of the floating battery thus constructed is rather weak, and consequently a coil of considerable length is required to make it sensitive. A better construction is that shown in figs. 435, 436, in which the extremities of the coil are connected with

Fig. 435.



Fig. 436.

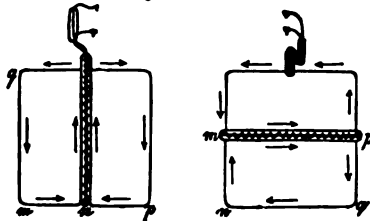


a small Daniell's cell contained in a wide glass tube attached to the cork float. With this arrangement, stronger acid may be used and a more energetic current obtained, so that a thinner coil, or even a single circular or rectangular wire, is sufficient to exhibit strong deflection under the influence of a magnet.

A movable electric current is deflected by the earth's magnetism as well as by an ordinary magnet. This may be shown either with Ampère's apparatus or with the floating battery, the wire of either of which, when left to itself, takes up a position at right angles to the magnetic meridian. If it be remembered that the north magnetic pole of the earth is analogous to the south pole of an ordinary magnet, it will be seen that, in the position of stable equilibrium, the direction of the current is from east to west in the lower horizontal branch, and from below upwards on the western vertical side.

The action of the earth on the current is much less energetic than that of a bar-magnet held near the wire; nevertheless it may sometimes interfere with the results of this latter action. This source of complication may be obviated by giving to the movable wire the form of a double rectangle, fig. 437, so arranged that the earth's action on the one half shall be neutralised by that on the other. Such an arrangement is called an *astatic conductor*.

Fig. 437.



## MUTUAL ACTION OF ELECTRIC CURRENTS.

*Electric currents moving in parallel lines attract one another if they move in the same direction, and repel one another if they move in opposite directions.*

This law may be demonstrated by bringing a conducting wire connecting the poles of a rather powerful voltaic battery near the wire of the floating battery, as shown in fig. 438, or the wire of Ampère's apparatus (figs. 433, 437).

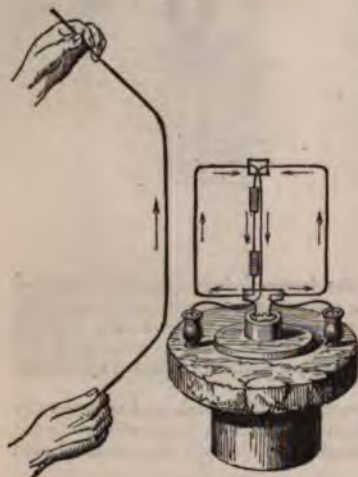


Fig. 438.

The mutual attraction and repulsion of currents is not, however, confined to the case of parallelism; for if two currents,  $\Delta$  B, are moving in directions inclined to each other in the same plane,  $\Delta$  may be resolved into two component currents, one perpendicular and the other parallel to B; the former produces no effect, because it is equally inclined to B both ways, and the latter attracts or repels B, according as it is moving in the same or the opposite direction. If the currents are in different planes, two such resolutions will show how much of the force of one may be considered as acting parallel to the other. The general result is, that two inclined currents attract each other if they both tend towards or both from the summit of the angle formed between them, and repel one another if one is approaching that summit and the other receding from it. The different cases of this action are shown in fig. 439. If a horizontal conducting wire be

Fig. 439.

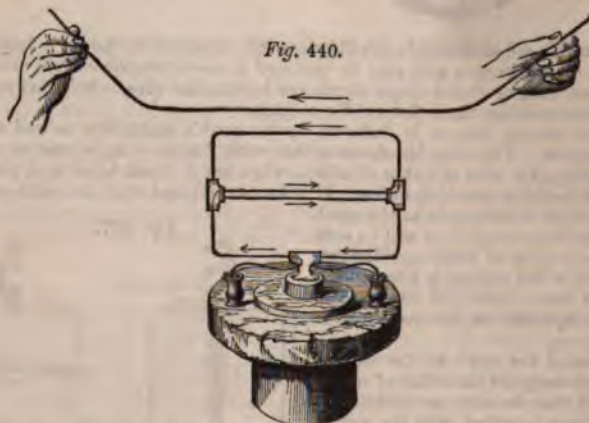
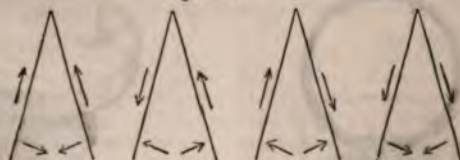


Fig. 440.

held over the horizontal branch of the wire of a floating battery (fig. 440), and inclined to it at any angle whatever, then if the two currents both approach the summit of that angle on one side and recede from it on the other, the floating battery will turn round, till the upper horizontal branch of its wire has placed itself parallel to the

other wire, and as near to it as possible, the two currents moving in the same direction, this being their position of stable equilibrium. If, on the other hand, the original position of the currents is such, that one approaches the summit of their angle of intersection and the other recedes from it, the wire of the floating battery is at first repelled and turns round, making a larger and larger angle with the fixed wire, till it ultimately settles itself in the position of equilibrium shown in the preceding figure.

Suppose now the wire of the floating battery to have the form of a helix, as in *fig. 441*, and that another helix also conveying an electric current is held over it. The floating helix will place itself parallel to the other, and in such a position that the currents in the nearest parts of the two run in the same direction; and a little consideration will show that if the helices are both right or both left-handed (*p. 444*), their similar ends, *i. e.* those by which the current enters or leaves the helix, will be placed in contrary positions, the positive end of one over the negative end of the other. Moreover, if the positive end of the one (that by which the current makes its exit) be presented to the negative end of the other, attraction takes place; whereas the two positive or two negative extremities or poles repel each other. In short, the two helices act upon one another just like two bar-magnets; and indeed if a magnet be substituted for the fixed helix, the floating helix will be attracted and repelled by it, and will place itself parallel to it, just as it behaves to the other helix. Moreover, if the floating helix be left to itself, it will take up a position in which the current runs from east to west, and the axis of the helix therefore points north and south, just like a magnet.



Fig. 441.

This striking resemblance between the mutual action of electric currents and that of magnets has led to the idea, suggested and developed by Ampère, that magnetism is actually produced by electric currents, circulating round the magnet in planes perpendicular to its axis, and such, that on looking along the axis of the magnet with its south pole turned towards the observer, the current moves in the direction of the hands of a watch, that is, from the left side through the top and down by the right through the bottom to the left again. Thus in the bar-magnet represented in *fig. 442*, the south pole is at the lower end. Whether such currents actually exist is more than we are at present prepared to say. No direct proof of their existence has yet been given; but the theory affords a simple and perfectly satisfactory explanation of all cases of the action of magnets on each other, and of the mutual action between the magnet and the electric current. The fundamental fact of electro-magnetism, *viz.* that a magnet tends to place itself at right angles to an electric current, is, according to this theory, a direct consequence of the tendency of electric currents to place themselves parallel to one another (see *fig. 442*).

The action of the currents circulating round the axis of a magnet is well illustrated by the following experiment:—Present a bar-magnet to a floating battery, with a flat circular coil (*fig. 435*), in such a manner that the currents of the magnet shall coincide in direction with that in the coil. The coil will be attracted by the magnet and move on to it, fixing itself exactly in the middle, where it is equally attracted both ways. Now take hold of the coil, withdraw the magnet, and insert it the contrary way. The coil, if exactly in the middle of the bar, will remain there in a position of unstable equilibrium; but if ever so little nearer to the free end of the magnet, it will shoot off, turn itself round, and then return to its position in the middle of the magnet.

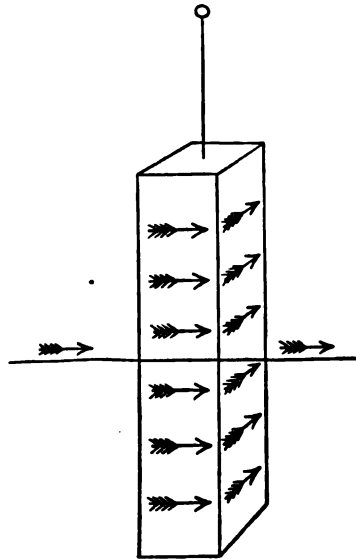
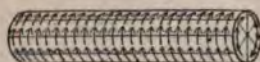
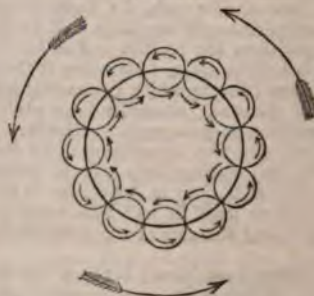


Fig. 442.



There are, however, certain phenomena into which we cannot here enter, relating to the mutual action of magnets and electric currents, which render it necessary to suppose that the currents which give rise to the polarity of magnets are molecular, that is to say, that they circulate round each individual particle of the magnet. These currents may be supposed to pre-exist in all magnetic bodies, even before the development of magnetic polarity, but disposed without regularity, so that they neutralise one another. Magnetisation is the process by which these molecular currents are made to move in one direction, so that those situated at the surface of the magnet yield as their resultant a finite current circulating round the magnet, while the currents in the interior are neutralised by those in the next external layer, the contiguous portions of which move in the direction opposite to their own. *Fig. 444* is a section of a cylindrical magnet showing the external layer of molecular currents, the observer looking

*Fig. 443.**Fig. 444.*

towards the north pole; and *fig. 443* shows the finite superficial currents produced by their joint action.

#### *Magnetisation by the Electric Current.*

A bar of iron, steel, or other magnetic body placed at right angles to an electric current, becomes magnetised, its poles being situated in the same direction as those of a magnetic needle subjected to the influence of the same current and in the same relative position, this direction being such that the currents which, in Ampère's theory, are supposed to circulate round the magnet, coincide in direction with the acting current on that side of the bar which is nearest to it.

Soft iron is easily magnetised by the electric current, but returns to its ordinary unmagnetised state as soon as the current ceases to act upon it; it therefore requires the action of a continuous current, like that of the voltaic battery. Steel, cast iron, and nickel, on the other hand, are more difficult to magnetise, but retain their magnetic power when removed from the influence of the current; the resistance which these bodies offer to any force tending to polarise them, is best overcome by electricity of high tension; — indeed hard steel never acquires its full magnetic polarity under the influence of currents of low tension, but only when subjected to the sudden discharge of a Leyden jar or battery (p. 398).

*Magnetisation of Soft Iron.*—A short bar of soft iron placed at right angles to a wire joining the poles of a voltaic battery becomes magnetic; and on bringing the same wire in contact with a mass of iron filings, a number of them will adhere to it as long as the circuit is complete, falling off as soon as it is broken. This attraction, according to Ampère's theory, is merely a case of mutual attraction between electric currents running in the same direction.

In longer bars of soft iron, the magnetic influence of a straight current is scarcely, if at all, perceptible; but by causing the current to act simultaneously all along the bar, which may be effected by coiling the wire round it in the form of a helix, very strong magnetic polarity may be developed, even by the current of a small voltaic couple. The wire, if covered with silk, may be coiled directly round the bar; if uncovered, it must be coiled round a paper or wooden tube within which the bar is inserted; but covered wires are generally used, because the turns of the coil may then be kept very close together, and the wire may be coiled round the bar in several layers. The direction of the polarity depends of course on the kind of helix used. With a left-handed helix (p. 444), the north pole of the bar is at that end of the coil at which the current enters.

A bar of soft iron bent in the form of a horse-shoe, and having a long coil of wire round it, becomes a very powerful magnet, when its poles are joined by a keeper of soft iron and a current is sent through the coil; such an electro-magnet will support a very great weight. If the soft iron is of good quality, and has been several times tempered by slow cooling, the development of the magnetism follows instantaneously on the closing of the circuit; by far the greater part of the magnetism disappears also on breaking the circuit, but a small amount is retained for a time, depending on the length of the bar—long bars, and more especially horse-shoes, retaining a portion of their magnetism for a longer time than short ones. In horse-shoes the retention of the polarity is greatly promoted by joining the poles with a soft iron keeper. A horse-shoe electro-magnet, which supported a weight of 120 lbs. while under the influence of the current, was found to carry 50 lbs. when the circuit was interrupted, and retained this power for a long time, while the keeper remained in position; but on forcibly separating the keeper, the whole of the magnetism was destroyed. The cause of this effect is that the keeper, by contact with the poles of the magnet, becomes itself a magnet, each of its extremities becoming a pole of opposite name to that of the magnet with which it is in contact; and these poles intensify the polarity of the magnet, just as a body electrified by induction intensifies the electric polarity of the inducing body (p. 386), the whole forming a kind of closed magnetic circuit, the different parts of which tend to keep one another in equilibrium; on removing the keeper, this equilibrium is destroyed, and the bar of iron returns to its ordinary state.

*Magnetisation of Steel.*—Steel bars or wires are permanently magnetised when placed within a helix through which a voltaic current or an electric discharge is passed. For the latter mode of operation, the helix must be coiled round a glass tube and the steel bar placed within the tube (p. 398); for the former, either this method may be adopted, or helices of covered wire without the glass tube may be used. With a simple helix, that is, one in which all the turns of the coil go the same way, the resulting magnet will have only two poles, like an ordinary bar-magnet, the north being turned towards the positive or negative end of the helix, according as the latter is right or left-handed; but if one half of the helix is right and the other left-handed, a kind of double magnet will be formed, having two similar poles at each end, and a contrary pole in the middle; and with a triple helix, *e.g.* consisting of a right-handed portion placed between two left-handed portions, a magnet will be formed with four consecutive poles, arranged thus, N, S, N, S; and similarly for any number of alternations.

By the discharge of a large Leyden jar or battery, steel wires may be magnetised when simply laid at right angles to a straight conducting wire, either in contact with it, or at the distance of several inches. The intensity of the magnetism thus developed increases with the intensity of the discharge, other things being equal; but when needles of hard steel are placed at different distances from the conducting wire, the intensity, and even the direction, of the magnetic polarity induced by the same electric discharge, are found to vary in a very remarkable manner, according to the distance. From the experiments of Savary (Ann. Ch. Phys. [2] xxxiv. 5), and Abria (*ibid.* [3] i. 385), it appears that the intensity of the magnetism produced by the electric discharge does not diminish constantly as the distance becomes greater, but increases with the distance beyond a certain point, where it is at a minimum; and that, on the same side of the conducting wire, and with the same direction of the discharge, the situation of the magnetic poles with regard to the wire changes more than once at different distances. In contact with the conducting wire, or at very short distances from it, the poles are disposed according to the general law (pp. 442, 444). The table on p. 450 contains the results obtained by Savary with a platinum wire 2 metres long and  $\frac{1}{4}$  millimetre in diameter, hard-tempered steel needles 15 mm. long and  $\frac{1}{4}$  mm. in diameter, and an electrical battery having a coated surface of 22 square feet. The strength of the magnetism acquired by the needles was estimated by the time in which they performed a given number of oscillations under the influence of terrestrial magnetism. To avoid any errors that might arise from the mutual action of the steel needles, they were not placed vertically one over the other, but over different parts of the conducting wire. The polarity of a needle is called *positive* when its direction coincides with the general law, *negative* in the contrary case.

It appears from the table that, for the positively magnetised needles, there was a maximum of intensity at contact, and another at the height of 30 mm. above the wire, the second maximum being somewhat greater than the first. For the negatively magnetised needles, there was a maximum at 5 mm. The minima of intensity corresponded with the changes of sign. In another experiment, in which the conducting wire was only 1 metre in length, four changes of direction in the polarity were observed, and the last maximum was at the height of 40 mm. instead of 30.

No. of Needle.	Distance from the Wire in Millimetres.	Time of 60 Oscillations.	Direction of the Poles.
1	0.0	52".4	Positive
2	1.2	1' 3".8	"
3	2.5	1' 12".8	Negative
4	3.7	44".6	"
5	5.0	40".0	"
6	6.0	41".8	"
7	7.4	44".8	"
8	8.5	58".2	"
9	9.7	1' 20".1	"
10	10.9	1' 52".0	Positive
11	11.8	1' 18".6	"
12	12.5	1' 1".0	"
13	13.8	49".6	"
14	16.3	38".2	"
15	18.7	33".8	"
16	21.0	31".3	"
17	23.8	29".5	"
18	28.5	30".8	"
19	34.0	29".8	"
20	46.0	35".9	"
21	70.0	55".6	"
22	100.0	1' 27".6	"
23	130.0	1' 48".0	"

The diameter of the conducting wire likewise affects the distances at which the changes of sign in the magnetic polarity take place; with a very fine wire,  $\frac{1}{8}$  mm. in diameter, no such changes of sign were observed, and the maximum of intensity was at the distance of 11 mm., that is to say, five times less than with a wire of three times the diameter.

The intensity of the magnetisation is, *ceteris paribus*, greater as the length of the wire is less in proportion to its diameter. This increase, however, has a limit: a wire 1 metre long, for example, gives the highest maximum of magnetisation when its diameter is  $\frac{1}{8}$  mm.; at the distance at which this maximum effect is produced, the needle is magnetised to saturation; with greater lengths of wire the intensity is less. The relative maxima are nearer to the wire in proportion as the wire is longer.

The influence exerted by the length and diameter of the conducting wire, appears to depend upon the amount of retardation which it produces on the discharge: for in a circuit formed of three wires of unequal diameters, joined end to end, the magnetising effect of the discharge is the same, in whatever part of the circuit the needle is placed, the velocity of the discharge being, of course, the same in every part of the circuit.

The dimensions and hardness of the needles have likewise a very decided influence on the results: needles of unhardened steel exhibit no change of sign, whereas those of hard-tempered steel exhibit at least three such changes. If the diameter of the needle is somewhat considerable, the strongest magnetisation takes place in contact with the conducting wire, and the intensity continually diminishes with increase of distance. A hardened needle of considerable thickness is magnetised by the discharge like an unhardened needle of smaller diameter, a fact which may be explained by observing that the hardening affects only the surface, and that, in a thick needle, the surface bears a smaller proportion to the mass than in a thin one.

With helices, also, several changes of sign were obtained in the polarity of hard-tempered steel needles placed at different distances; but when the total length of the wire was increased without changing that of the coiled portion, the changes of sign became less frequent, till finally the polarity was no longer reversed at different distances, but only became less intense as the distance increased. The length of a needle placed within the helix has no influence on the direction of its polarity, but only on the intensity.

Non-conducting bodies, such as dry paper, wood, or glass, interposed between the steel bars and the conducting wire, have no influence, either on the direction or on the intensity of the magnetism produced, but conducting bodies modify the effect to a considerable extent; thus, if two similar needles are placed within a helix, one un-



covered, the other enclosed in a thick copper cylinder kept out of contact with the helix, a discharge which magnetises the former strongly, produces no effect on the latter. By gradually diminishing the thickness of the metallic envelope, the needle is more and more magnetised by a discharge of given strength. In some cases, the envelope changes the direction of the polarity induced. It is only by continuous envelopes that these effects are produced; metallic powders, which conduct but slowly, have no effect.

These effects, and others produced by the interposition of metallic discs, are due to momentary electric currents, excited in the conducting disc or envelope by the discharge. The remarkable variations of intensity and inversion of the polarity at different distances from the wire, are probably due to a similar cause, namely, the polarisation of the molecules of the intervening medium.

Savary has also shown that similar results may be obtained with the continuous voltaic current, and that the magnetising effects of the current approach more nearly to those of the sudden discharge, in proportion as the current has a higher intensity, and the battery is charged with a liquid of less conducting power. Altogether, the effects are less distinct with the current than with the sudden discharge, especially with regard to the change of direction of the polarity at different distances from the conducting wire. Steel needles are not strongly magnetised by the current unless they are placed within a helix.

#### ELECTRO-DYNAMIC INDUCTION.—MAGNETO-ELECTRICITY.

An electric current produces no perceptible disturbance in the electric state of a neighbouring conductor, so long as it remains of constant strength, and the relative positions of the two remain unaltered; but if the current undergoes any variation of strength—especially, therefore, at the moments of its commencement and cessation,—or if it be made to approach or recede from the other conductor, it then produces an electrical disturbance in that body, and if the latter forms a closed circuit, develops in it a current of electricity. This mode of action, discovered by Faraday in 1832, is called *Electro-dynamic Induction*. Its effects may be studied by means of the apparatus, represented in *fig. 445*.

Two copper wires covered with silk are coiled round a hollow wooden cylinder, so as to form two perfectly similar but separate helices, the turns of which are parallel, and as close to each other as possible. The ends of one of these helices A, are connected with a galvanic battery; those of the other, B, with a galvanometer. At the moment of completing the battery circuit, the galvanometer needle moves, its motion indicating a current in the wire B, in the direction opposite to that of the battery current in A. This induced current, however, is only momentary, the needle immediately returning to its ordinary position of equilibrium, and remaining there as long as the battery circuit remains closed; but on breaking the circuit, the needle again moves, and in the direction opposite to that of its first movement, indicating, therefore, a current in the wire B, in the same direction as that in A; this last also is only momentary.

Any variation in the strength of the battery current produces effects similar in kind, though less in degree, to those resulting from its commencement or cessation: for an increase in the strength of a current is equivalent to the production of a fresh current; and a decrease, to the cessation of a current of less strength.

If only a single helix is wound round the hollow wooden cylinder in the last figure, its ends connected with a galvanometer, and another helix through which a current is passing is quickly thrust into the tube: a momentary current is also induced in the first helix in a direction opposite to that in the second; so long as the latter remains within the tube, no current passes through the galvanometer, but on quickly withdrawing the inner helix, a momentary current passes through the galvanometer, in the direction opposite to the former, that is to say, in the same direction as that in the movable helix. This experiment is, indeed, only another form of the first; in both

*Fig. 445.*



cases an electric current is suddenly brought into the neighbourhood of a conducting wire forming a closed circuit, and as suddenly withdrawn; but the making and breaking contact with the battery in the first experiment, admits of a much quicker introduction and removal of the current, than the mechanical movement of the helix in the second: hence the induced currents are more powerful in the first instance.

All these effects are greatly intensified, but not altered in direction, by the introduction of a bar of soft iron or a bundle of iron wires within the inducing helix. Thus with the double helix (*fig. 445*), on making contact with the battery, the iron becomes strongly magnetised, and we may suppose that a number of molecular currents are made to circulate round its particles in the same direction as the current of the helix A (*p. 447*); these, at the moment of their formation, induce a strong momentary current in the contrary direction in the helix B; and on breaking contact, the magnetism is destroyed, and an equally strong current is induced in B, in the same direction as that in A.

The same effects are produced by magnetising the iron bar within the helix in any other way; thus on bringing the opposite poles of two bar magnets in contact with the extremities of the bar, a current is developed in the helix B; and on removing the magnets and thereby unmagnetising the bar, a momentary current is formed in the contrary direction.

Again, in the second form of the experiment, if a bar of soft iron is introduced into the movable helix, a current is developed in the fixed helix in the same direction as when the iron is not there, but of greater intensity; and if, instead of the helix, a permanent magnet be thrust into the tube with its poles in the same direction as those of the temporary magnet formed by the helix, the same momentary current will be produced as before, and a contrary current on withdrawing the magnet.

The direction of a current developed by the action of a magnet, is determined by the following law:—*The development of magnetism in a bar of iron in the neighbourhood of, and at right angles to a closed conducting wire, or the movement of a permanent magnet in the neighbourhood of such a wire, induces in it a current of electricity, the direction of which is opposite to that which would develop the same magnetic polarity in the iron, or impress the same motion on the magnet; and on destroying the magnetism in the iron, or moving the permanent magnet the contrary way, an opposite current is developed in the wire.*

The intensity of the induced currents varies with the length and diameter of the wire in which they are developed, also on the energy of the inducing currents, or the power of the magnet. In general, it is advantageous to use very long wires, and even to join several helices end to end; but in that case, if the induction is not effected by the action of a magnet, it is necessary to employ an inducing current proceeding from a battery of a considerable number of pairs. These conditions vary, however, according to the effects to be produced, and consequently with the nature of the conductors through which the induced current is to pass.

An electric current, at the moments of its commencement and cessation, develops momentary currents, not only in neighbouring wires, but likewise in the wire through which itself is passing. When a copper wire is made to dip into two mercury cups attached to the plates of a simple voltaic battery, the spark produced on breaking contact is much brighter than that formed on making contact, especially if the wire is long and formed into a coil, and still more if it is coiled round a bar or horse-shoe of soft iron. The cause of this difference is that the battery current, at the moment of its commencement, induces an opposite current in the conducting wire, whereby its own force is partly neutralised, whereas at the moment of cessation, it induces a secondary current in the same direction as itself, whereby its force is augmented and a stronger spark produced.

These secondary currents, which, like those induced by the current in neighbouring wires, are of considerable intensity, may be rendered evident by attaching to the wire, near its extremities, two thinner wires connected with a galvanometer; the needle will then be deflected on completing and breaking the battery circuit. If the extremities of these thinner wires are brought close together, a spark will pass between them at each completion and interruption of the circuit; and if copper cylinders are attached to them and held in the moistened hands, a shock will be felt. When the secondary current is diverted in either of these ways, the brightness of the spark which appears on breaking the battery circuit is much diminished.

The formation of these secondary currents, called extra-currents, will be easily understood if we remember that a wire may be regarded as a number of smaller wires or rows of particles laid parallel to one another.

Induced currents are also developed by the influence of the earth's magnetism,



*e.g.* when a rectangular wire whose extremities are connected with a galvanometer is made to move round its lower side at right angles to the magnetic meridian. The direction of the current, in all varieties of the movement and form of the conductor, may be easily made out from the preceding general rules, remembering that the north magnetic pole of the earth is analogous to the south pole of an ordinary magnet.

*Induced currents of higher orders.*—An induced current is capable of developing other induced currents in neighbouring conductors; and these again develop others, the series being continued through several terms. These phenomena were first observed by Dr. Henry, of Princeton (Ann. Ch. Phys. [3] iii. 394), who made use of the apparatus represented in *fig. 446*, consisting of a number of flat spirals of covered

*Fig. 446.*



copper riband. The first spiral *a*, is connected with the poles of a voltaic battery; above this, and very close to it, is placed another spiral *b*, the ends of which are connected with those of a third spiral *c*, above which, and very close to it, is a fourth spiral *d*, connected with a fifth *e*, and so on. At the moment of *interrupting* the battery current in *a*, an induced current is developed in *b* in the same direction as in *a*; this induced current passes on to *c*, and there develops in *d* a momentary current in the contrary direction; this current passes on to *e*, where it develops in *f* a current whose direction is opposite to that of *d*, and therefore the same as that of *a* and *b*. The direction of the current in any one of the spirals may be determined by interposing in its circuit a galvanometer, or a chemical voltameter, or, as in the figure, a helix containing a steel wire, which becomes magnetised, and indicates the direction of the current by the positions of its poles.

Of the induced currents developed on *interrupting* the primary or battery current, the secondary, quaternary, and all of even order, have the same direction as the primary current, while the tertiary, and others of uneven order, move in the contrary direction.

Similar phenomena are observed at the instant of *closing* the battery circuit, excepting that as the secondary current (in the helix *b* above) is of contrary direction to the primary, all the induced currents of even order also move in the direction contrary to that of the primary, and those of uneven order in the same direction as the primary current.

The phenomenon is, however, more complicated than the preceding description would imply: for every current, however developed, induces in a neighbouring conductor two other currents, one at the moment of its commencement, in the opposite direction to itself, the other at the moment of its cessation, in its own direction. Hence there are in reality, two secondary, four tertiary currents, eight of the fourth order,  $2^{n-1}$  of the  $n$ th order. It is only, however, the secondary currents that are separated from each other by a finite interval, that namely between the closing and interruption of the battery circuit, which may be made as long as we please; but each of the secondary currents has but a momentary duration: consequently, of the two tertiary currents which it produces, the second follows instantly upon the first, and the current actually observed is merely the difference between the two. Similarly with regard to the currents of higher orders. If then the two currents developed in a conductor at the same instant by the action of a current of the next lower order, were always equal in quantity and intensity, no currents of higher order than the second could ever be observed. This, however, is not the case; the two secondary currents formed at the commencement and cessation of the primary current are equal in quantity, producing equal and opposite deflections of the galvanometer; but they differ in intensity, that is to say, in their power of overcoming resistances, the direct current having a greater intensity than the inverse. Similar differences of intensity appear also to exist in the two simultaneous currents of any higher order, excepting that in these the inverse currents possess the higher intensity, so that the current actually produced



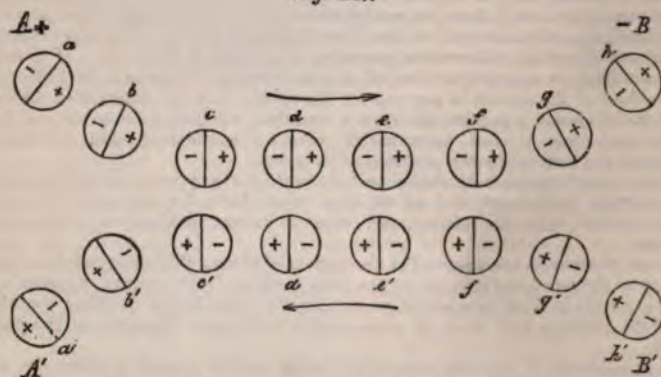
moves in the direction contrary to that to which it owes its origin. That the induced currents of orders higher than the second are really the resultants of opposite induced currents of different intensity, is in accordance with the fact, that they are all capable of producing chemical, calorific, and physiological effects, that is, of traversing circuits which offer considerable resistance, but that the galvanometer is scarcely deflected by any induced current of higher order than the second.

Induced currents of several orders are likewise produced by the sudden discharge of electricity, as by the discharge of an electrical battery. The effects are somewhat complicated, but the general laws of the action are the same as when the primary current is continuous. As, however, the primary discharge is instantaneous, or nearly so, the two opposite secondary currents which it induces on a neighbouring conductor, succeed one another at an imperceptibly short interval, and therefore nearly neutralise each other, if the circuit does not present much resistance; but if the circuit is interrupted, either by a thin wire which becomes heated, or by an interval which gives rise to the passage of a spark, one of the induced currents, generally the second, or that which has the same direction as the primary, predominates over the other. (Riess, *Reibungs-electricität*, ii. 266-355.—Matteucci, *Ann. Ch. Phys.* [3] iv. 153.—Dove, *ibid.* iv. 336.—Marianini, *ibid.* x. 491; xi. 385.—Knochenhauer, *ibid.* xvii. 130.—Vérdet, *ibid.* xxiv. 377.—De la Rive, *Traité* i. 406.)

*Theory of Electro-dynamic Induction.*—The following explanation of the development of induced currents is given by De la Rive (*Traité* i. 445). Electro-dynamic induction may be regarded as the result of the decomposition by influence of the natural electricity belonging to each particle of the conductor subjected to the action of the current, by the already separated electricities of each particle of the conductor conveying that current.

Considering the current as a series of decompositions and recompositions of the electricities of contiguous molecules, suppose AB (*fig. 447*) to be a conductor through

Fig. 447.



which a current is passing from A to B. The particles which compose this conductor have their natural electricity decomposed, the  $-E$  of each turning towards A, which is the positive pole of the apparatus generating the current, and the  $+E$  to B, which is the negative pole. These opposite electricities, as soon as they are separated, recombine from particle to particle, the  $-E$  of  $a$  with the  $+E$  of the pole A, the  $-E$  of  $b$  with the  $+E$  of  $a$ , and so on up to  $h$ , the  $+E$  of which unites with the  $-E$  of the pole B. This recombination, which is instantaneous, is immediately followed by a new decomposition, then follows another recombination, &c. this series of actions going on so rapidly that, as experiment shows, the whole of the conductor is kept in a constant state of tension.

Now let there be a second conductor,  $A'B'$ , as near as possible to the first, but insulated from it by silk or wax. At the moment when the current begins to pass through AB, and its particles are polarised, as in the figure, those of  $A'B'$  become polarised in the opposite way, the  $+E$  of each particle of  $A'B'$  being opposite to the  $-E$  of the corresponding particle of AB; whence it follows that, if at the moment when the current begins to pass through AB, the two extremities of  $A'B'$  are united by a conductor, such as a galvanometer-wire, the  $+E$  of the particle  $a'$  unites through that conductor with the  $-E$  of the particle  $h$ , producing therefore a momentary current whose direction is from  $A'$  to  $B'$  in that conductor, and from  $B'$  to  $A'$  in the wire  $A'B'$

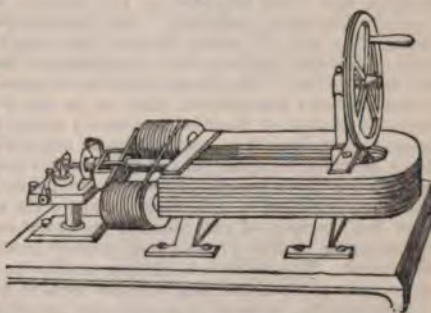
itself, that is to say, in the direction contrary to that of the inducing current. In like manner, if the ends  $A' B'$ , instead of being joined by a conductor, are made to communicate severally with the two plates of a condenser,  $A'$  imparts to it a charge of  $+E$ ,  $B'$  a charge of  $-E$ . As soon as  $a'$  has lost its positive and  $b'$  its negative electricity, the  $-E$  of  $a'$  is disguised by the  $+E$  of  $b'$ , and so on to  $g'$ , the  $-E$  of which is disguised by the  $+E$  of  $h'$ . These opposite electricities attached to the contiguous particles do not at once recombine and neutralise one another, because they are retained in their places by the opposite electricities of the particles of  $AB$ ; but as soon as the current ceases to pass along  $AB$ , the  $-E$  of  $a'$  unites with the  $+E$  of  $h'$  through the medium of the conductor which connects the ends  $A', B'$ , and at the same time, the opposite electricities of the particles  $a', b', c', d', e', f',$  and  $g'$  recombine, producing a current from  $B'$  to  $A'$  in the conductor, and from  $A'$  to  $B'$  in the wire itself, that is to say, in the same direction as the primary current in  $AB$ . The state of tension of the wire  $A' B'$  during the time that the current is passing through  $AB$ , is that which Faraday calls the *electrotonic state*; its creation produces the first induced current, and its cessation, the second.

This mode of explanation is not however very satisfactory, and it does not show clearly why the secondary currents are produced only at the commencement and cessation of the primary current, and not during its continuance. Supposing a molecular polarisation, like that represented in *fig. 447*, to be produced in the two wires, a discharge ought to occur in  $A' B'$  at the same instant as in  $AB$ , then a second decomposition of electricities, then a second discharge, and so on, as long as the current in  $AB$  continues. In short, all the changes of state in  $AB$  ought to be reproduced in  $A' B'$ , inversely and with less intensity. More complete theories of electro-dynamic induction have been given by Weber (*Pogg. Ann.* lxxiii. 193), and Neumann, (*Abhandl. d. Berl. Acad.* 1845, 1, and 1847, 1); but they are not of a nature to be introduced into this work. (See Wiedemann, *Galvanismus*, &c. ii. 675; Müller, *Lehrbuch*, ii. 378.)

*Magneto-electric Machines.*—The preceding principles have been applied to the construction of machines for the rapid and continuous development of induction currents. All these machines depend upon the rapid magnetisation and demagnetisation of a bar of soft iron round which a continuous wire is coiled, the development and destruction of the magnetism being effected, either by giving the bar of iron a continuous motion, which causes it to pass at short intervals before a magnetic pole,—or by subjecting it to the influence of an electric current, the circuit of which is completed and broken at very short intervals.

Saxton's magneto-electric machine (*fig. 448*) consists of a strong horse-shoe magnet, fixed horizontally, and a soft iron keeper in the form of a horse-shoe, each arm of which is encircled by a silk-covered wire. The keeper is made to revolve on a horizontal axis by an endless cord passing round a wheel, whereby the two extremities of the keeper are brought in front of the poles of the magnet twice at each turn of the wheel. By this motion, the keeper is alternately magnetised and unmagnetised. When it is in the *axial* position, that is to say, when its ends face the poles of the magnet, as in the figure, it is magnetised; when it has got a quarter round, or into the *equatorial* position, it is unmagnetised; when half round, it is again a magnet, but with its poles in the reverse of their former direction; when three-quarters round, it has again lost its magnetism, and so on. Now, as the loss of one kind of magnetic polarity is the same as the gain of the opposite kind, it is easy to see that, at each complete turn of the wheel, there will be two currents in opposite directions developed in each of the coils of wire. Further, on comparing each of the induced currents in one of the wires, with that which is induced at the same instant in the other wire, it is clear that these two currents must move in contrary directions, since the magnetic poles to which they owe their origin are of opposite kinds. Hence, to enable these currents to unite their forces instead of neutralising each other, it is necessary to join together the two ends of each of the wires from which the current appears to issue, and the two by which it appears to enter at the same time; these four ends thus joined two and two, present but two extremities or poles, which may be connected with the body through which the induced

Fig. 448.





currents are to be sent. Another mode of connection is to join the extremity of one wire from which the current issues, with that extremity of the other at which it enters, at the same instant leaving the other ends free to form the poles. These two arrangements differ in this respect, that in the former there are two parallel circuits, the effects of which are added together, whereas in the second, there is only one circuit twice as long as the former. The second circuit has evidently much less conducting power than the first, which consists of two wires only half as long as the single wire of the second; it is therefore the arrangement to be preferred when the induced currents are intended to pass through imperfect conductors, or interruptions in the circuit.

To establish the connections between the two extremities or poles of the wire, one of them is brought in contact with a metal rod fixed on the prolongation of the axis in the middle of the keeper, and moving with it,—the other with a vertical metal disc fixed by its centre to the same rod, which passes through it, but is well insulated from it by a glass tube enveloping the rod. The disc dips constantly by its lower part into a little trough of mercury, which also receives in succession the two points of a little brass needle attached to the end of the rod, and in metallic communication with it. Every time, therefore, that one of the points of the needle is brought by the rotation into such a position as to dip into the mercury, a metallic communication is established between the extremities or poles of the two coils of wire. If the needle is adjusted so that each of its points shall dip into the mercury just as the keeper arrives in front of the poles of the magnet, and emerge as it quits them, the first induction current is developed at the moment of immersion, the second at the moment of emersion. Both the immersion and the emersion are therefore accompanied by an electric spark, so that a constant succession of bright sparks is produced as long as the rotation of the wheel is continued.

To send the induced currents through any required conductor, the needle is removed, and the pointed end of a small metallic rod, firmly fixed to the frame of the apparatus, is pressed against the extremity of the axis of rotation, which is hollowed out for the purpose, the other end of the rod dipping into a cup of mercury. When the mercury in this cup and that in the basin, into which the disc above mentioned constantly dips, are connected by any conductor, the induced currents must necessarily pass through that conductor. To render the connection perfect, the bottom of the cavity at the end of the axis is amalgamated.

Magneto-electric currents are similar in most of their effects to voltaic currents; they heat thin wires to redness, decompose acidulated water, and give powerful shocks. To produce this last effect, two wires attached to metal cylinders (*fig. 449*) are connected, one into the mercury in the little cup, the other with that into which the disc dips; the cylinders are held in the hands, previously slightly moistened with salt water.

Magneto-electric currents differ however from voltaic currents in being discontinuous, and when produced by the machine above described, in moving in two opposite directions alternately. This discontinuity is the cause of the powerful shocks which they give; a voltaic current, the circuit of which is rapidly completed and broken, likewise produces much more powerful shocks than a continuous current from the same battery. The alternate movement of the magneto-electric currents in opposite directions has a considerable effect on its power of chemical decomposition: for this repeated change of direction necessarily causes a mixture of oxygen and hydrogen gases to be evolved from each electrode; and if the surface of the electrodes is rather large, considerable quantities of these mixed gases recombine and form water, especially when the alternate currents succeed each other very rapidly, so that the two gases are presented to each other almost in the nascent state. Hence it may happen that the quantity of gas collected in the voltameter is very small, although the currents may be very powerful, and produce great heat in metallic wires interposed in the circuit. These alternate currents produce no deflection of a galvanometer needle: whence we may conclude that they are equal in quantity.

It is possible, however, to arrange the interruptions of the circuit in such a manner as to produce a series of currents all in one direction. This is effected in Clarke's magneto-electric machine (*fig. 449*). The magnet *A* is vertical, and the connections are made without mercury, by means of a small steel spring *O*, pressing against a metal cylinder *K*, fixed upon the axis in place of the vertical disc in Saxton's machine, and insulated by a glass or wooden tube. Near the extremity of the axis is fixed another cylinder *H*, serving as a contact-breaker, for which purpose its surface is formed half of metal and half of wood, so that a second spring *Q*, which presses constantly against it, is brought in contact, as the axis revolves, sometimes with the metal, sometimes with the wood, and consequently is sometimes in, sometimes out of communication with one of the extremities of the coil, whilst the other spring, pressing constantly against the other cylinder *K*, which has a continuous metallic surface, is always in contact with the other end of the coil. To obtain a



succession of currents all in the same direction, it is only necessary to fix the disc H in such a manner that the spring may press against the metal part of its surface, while the keeper is passing from one axial position to the opposite, and against the wood during the other half of the revolution. By this arrangement, one of the opposing currents is cut off at every turn of the wheel, and a rapid succession of currents is sent through the wire, all in one direction, and capable of producing all the effects of the continuous current of a voltaic battery of high tension, the resemblance between the two being greater as the momentary currents succeed one another with greater rapidity. When, however, the length and tenuity of the wire exceed a certain limit, the induced currents are no longer capable of heating wires or decomposing electrolytes, but their physiological effects become more intense. These differences depend upon the relative conducting power of different parts of the circuit, and on the quantity of electricity in the currents. When the wire is very long and thin, and consequently offers considerable resistance to the passage of electricity, the currents are small in quantity but of high intensity.

*The Induction-coil.*—The most powerful of all magneto-electric machines are those in which the soft iron is magnetised and unmagnetised, not by moving in front of a permanent magnet, but by the action of an electric current, the circuit of which is completed and broken in rapid succession. These instruments, called induction-coils, offer considerable variety in the details of their construction, but they all consist essentially of a hollow cylinder containing a bar of soft iron or a bundle of iron wires, and having two helices of wire coiled round it, as in *fig. 445*, one connected with the poles of a voltaic battery, the other serving for the development of the induced currents. The alternate interruption and closing of the battery-circuit may be effected by means of a metal spring connected with one end of the battery-coil,

and pressing against the circumference of a toothed wheel, the axis of which is connected with the other end of the same coil, so that, as the wheel is turned round, the end of the spring is sometimes in contact with the teeth and completes the circuit, sometimes passes between them and interrupts it; but it is generally better to adopt a self-acting arrangement, as in the apparatus of Bonijol represented in *fig. 450*. In this machine, a fixed curved rod of metal, A B, and an elastic riband, C D, are interposed in the circuit of the inducing or battery current. The riband, by its elasticity, presses against the end B of the metal rod, and the two surfaces of contact are covered with discs of platinum to prevent oxidation. The elastic riband is pierced at E by a rod which can be raised or lowered, so as to bring its lower extremity, to which is attached a horizontal disc of iron, to a convenient distance from the bundle of wires in the axis of the cylinder. On making contact with

Fig. 449.

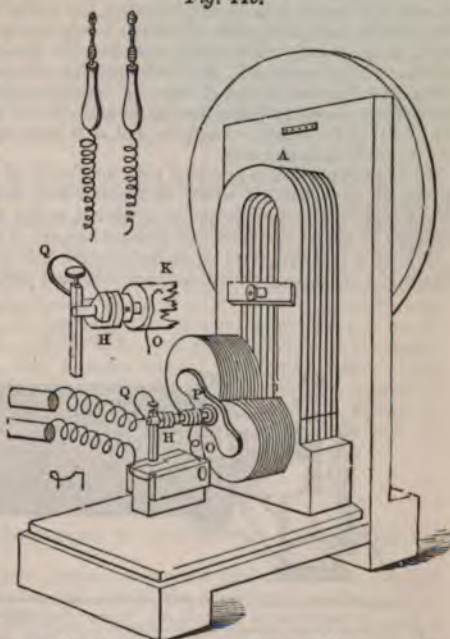


Fig. 450.

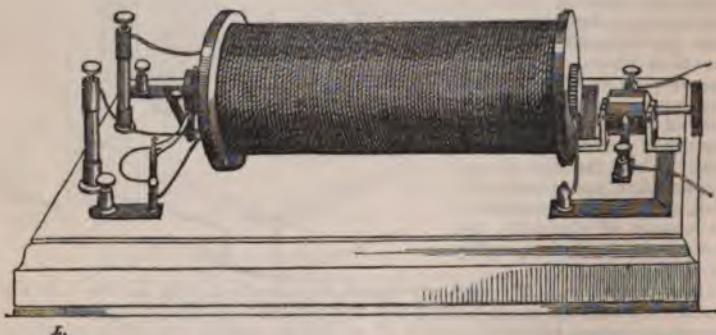


the battery, the soft iron core of the cylinder becomes magnetised, and attracts the little disc of iron, which pulls the elastic riband along with it, and separates the surfaces B, D, thereby breaking the circuit. As soon as this takes place, the iron wires lose their magnetism, the iron disc is no longer attracted, and the elasticity of the riband C D forces it up again, bringing the surfaces B, D in contact and completing the circuit: and this series of actions being repeated with great rapidity, an equally rapid series of induced currents is produced in the other helix, the ends of which communicate with the wires F, G. Consequently, any conductor, metallic, electrolytic, &c. interposed between F and G receives these induction currents. One of the poles of the battery is connected with the end H of the inducing coil, and the other with the end C of the elastic riband, the rod A B being connected by a wire with the other end K of the inducing coil.

The apparatus is also provided with another kind of current-breaker, consisting of a spring, M, and a toothed wheel, N, which is used when the self-acting current-breaker above described cannot be made available, as for example when the inducing coil is required to act on the other coil without the aid of the soft iron core.

The most powerful form of induction-coil, that of Ruhmkorff (*fig. 451*), acts by means of a self-acting current-breaker, like that just described. The cylinder of this

*Fig. 451.*



machine is a foot or eighteen inches long, and is surrounded by a coil of thick wire to convey the inducing current, and a much longer coil of thin wire for the development of the induced currents. The wires are insulated with resin, and the direction of the inducing current can be changed at pleasure by a commutator. To increase its power, M. Fizeau has added to it a condenser, consisting of two metallic ribands bent one round the other, and separated by oiled silk; these ribands communicate with the two extremities of the inducing wire, and thus become charged when the circuit is broken, and discharged when it is completed; this discharge, being in the same direction as the current, greatly increases its power.

In all these induction apparatus, a bundle of wires is much more effective in developing the induced currents than a solid cylinder of iron, apparently because, in the latter, superficial currents are developed by the action of the inducing current, which interfere with the principal effect. See *Dela Rive (Traité, i. 422)*.

The currents developed by the induction-coil, especially of Ruhmkorff's construction, are of very high intensity, capable of giving long sparks, and shocks of unendurable force. They are also capable of igniting gunpowder and other inflammable substances, and the apparatus has been used for exploding charges of gunpowder for mining, engineering, and military purposes. For military purposes, however, especially for operations in the open field, the use of the voltaic battery is attended with some inconvenience; and Messrs. Wheatstone and Abel have succeeded in producing the same effects by means of a magneto-electric machine, in which the currents are developed by mechanical movement, as in Saxton's and Clarke's machines. The apparatus contrived by Mr. Wheatstone for this purpose, consists of six small magnets, the poles of which are fixed soft iron bars, surrounded by coils of insulated wire. The coils of all the magnets are united together, so as to form, with an external conducting wire and the earth, a single circuit. An axis carries six soft iron armatures in succession before each of the coils. By this arrangement, all the magnets charge the wire simultaneously, and produce the effect of a single magnet of more than six times

the dimensions; and six currents are generated during a single revolution of the axis, so that with the aid of a multiplying motion applied to the axis, a very rapid succession of currents is produced.

Gunpowder alone may be fired by the magneto-electric discharge, especially when its conducting power is increased by the presence of a small quantity of moisture. Better results are, however, obtained by the use of fuses containing more inflammable substances, such as fulminating mercury. But the best mixture for the purpose is that invented by Mr. Abel, consisting of a mixture of phosphide of copper (p. 73) with chlorate of potassium, and a small quantity of cuprous sulphide, to increase its conducting power. For the description of the fuses used, and other details of the apparatus and manipulations, see Abel (Chem. Soc. J. xiv. 180).

#### MEASUREMENT OF THE FORCE OF ELECTRIC CURRENTS.

*Ohm's Formula.*—The amount of electric or chemical power developed in the voltaic circuit, or, in other words, the quantity of electricity which passes through a transverse section of the circuit, in a unit of time, evidently depends upon two conditions; viz., the power, or electromotive force of the battery, and the resistance offered to the passage of the current by the conductors, liquid or solid, which it has to traverse. With a given amount of resistance, the power of the battery is proportional to the quantity of electricity developed in a given time; and by a double or treble resistance, we mean simply that which, with a given amount of exciting power in the battery, reduces the quantity of electricity developed, or work done, to one-half or one-third. If, then, the electromotive force of the battery be denoted by  $E$ , and the resistance by  $R$ , we have, for the quantity of electricity passing through the circuit in a unit of time, the expression:

$$q = \frac{E}{R} \dots \dots (1)$$

This is called Ohm's law, from the name of the distinguished mathematician who first announced it.

By means of the formula (1), we may estimate the effect produced on the strength of the current by increasing the number and size of the plates of the battery. The resistance  $R$  consists of two parts; viz. that which the current experiences in passing through the cells of the battery itself, and that which is offered by the external conductor which joins the poles; this conductor may consist either wholly of metal, or partly of metal and partly of electrolytic liquids. Let the resistance within the battery be  $r$ , and the external resistance  $r'$ ; then, in the one-celled battery, we have

$$q = \frac{E}{r + r'} \dots \dots (2)$$

Now suppose the battery to consist of  $n$  cells perfectly similar; then the electromotive force becomes  $nE$ , the resistance within the battery  $nr$ ; if, then, the external resistance remains the same, the strength of the current will be denoted by

$$q = \frac{nE}{nr + r'} = \frac{E}{r + \frac{r'}{n}} \dots \dots (3)$$

If  $r'$  be small, this expression has nearly the same value as  $\frac{E}{r + r'}$ ; that is to say, if the circuit be closed by a good conductor, such as a short thick wire, the quantity of electricity developed by the compound battery of  $n$  cells, is sensibly the same as that evolved by a single cell of the same dimensions. But if  $r'$  is of considerable amount, as when the circuit is closed by a long thin wire, or when an electrolyte is interposed, the strength of the current increases considerably with the number of plates. In fact, the expression (3) is always greater than (2); for:—

$$\frac{nE}{nr + r'} - \frac{E}{r + r'} = \frac{(n-1)Er'}{(nr + r')(r + r')}$$

a quantity which is necessarily positive when  $n$  is greater than unity.

Suppose, in the next place, that the size of the plates is increased, while their number remains the same. Then, according to the chemical theory, an increase in the surface of metal acted upon must produce a proportionate increase in the quantity of electricity developed, provided the conducting power of the circuit is sufficient to give it passage. According to the theory which attributes the development of the electricity to the contact of dissimilar metals, an increase in the size of the plates does not



increase the electromotive force, but it diminishes the resistance within the cells of the battery by offering a wider passage to the electricity. Hence in the single cell, if the surface of the plates, and therefore the transverse section of the liquid, be increased  $m$  times, the expression for the strength of the current becomes:

$$\frac{E}{\frac{r}{m} + r'} = \frac{mE}{r + mr'}$$

If  $r'$  be small, this expression is nearly the same as  $\frac{mE}{r + r'}$ , that is to say, the quantity of electricity in the current increases very nearly in the same ratio as the size of the plates; but when the external resistance is considerable, the advantage gained by increasing the size of the plates is much less.

We may conclude, then, that when the resistance in the circuit is small, as in electro-magnetic experiments, a small number of large plates is the most advantageous form of battery; but in overcoming great resistances, power is gained by increasing the number rather than the size of the plates.

We have seen that the chemical or electrolytic power of a voltaic current is proportional to the amount of chemical action which goes on in the battery, and that the quantities of different electrolytes decomposed by the same current, are to one another as the weights of their comparable molecules (p. 439). Hence the chemical power of any current may be measured by the quantity of gas collected in a given time in a voltmeter placed in the circuit.

But it is by no means evident that the magnetic, calorific, and other effects of the electric current are proportional to its chemical power, and even if they were, the voltmeter would not afford a convenient measure of them, since, besides being somewhat uncertain in its indications, in consequence of the absorption and partial recombination of the oxygen and hydrogen evolved, it requires a certain time to elapse before a sufficient quantity of gas is collected for measurement, and cannot therefore give notice of any momentary variations in the power of the current. Hence to obtain exact measurements of the magnetic force of a current, it is necessary to resort to the magnetic action itself; instruments for this purpose are called Galvanometers or Rheometers. The so-called galvanometers, already described (p. 443), are really only galvanoscopes or multipliers; they indicate with great delicacy the existence and direction of a current, but are not adapted for quantitative measurement.

*The Tangent Galvanometer or Tangent Compass.*—In the true galvanometer (fig. 452) the current, instead of passing through a long coil of wire placed close to the needle, is made to pass through a broad circular band of brass or copper P Q, of considerable dimensions, in the centre of which is placed a magnetic needle  $n$ , the length of which is very small in comparison with the diameter of the circular conductor (it should not exceed  $\frac{1}{10}$ ), so that the distance of the extremity of the needle from the conductor P Q, and consequently the force exerted upon it by the current, may be sensibly the same at all angles of deflection. The instrument is placed so that the plane of the circle P Q coincides with the magnetic meridian.

To determine the relation which exists under these circumstances between the deflection of the needle and the force of the current, let N S (fig. 453) represent a long horizontal wire stretched in the direction of the magnetic meridian, and suppose a magnetic needle, placed with its centre vertically under the wire, to be deflected by a current passing along the wire in the direction  $ns$ , making an angle  $\phi$  with the wire. The current impels the pole  $s$  in the direction  $sf$ , perpendicular to N S, while the earth's magnetism acts upon it in the direction  $sg$  parallel to N S. Let the lines  $sf$ ,  $sg$  be taken proportional to the magnitudes of these two forces; draw  $asb$  perpendicular to  $ns$ , and  $fba$  parallel to it. Then the lines  $sa$ ,  $sb$  represented the components of the forces  $sf$ ,  $sg$  acting at right angles to the needle, and tending to move it one way or the other; hence, to keep the needle at rest,  $sa$  must be equal to  $sb$ . Now  $sa = sg \sin \phi$  and  $sb = sf \cos \phi$ ; therefore the condition of equilibrium is:

$$\begin{aligned} sf \cos \phi &= sg \sin \phi; \\ \text{therefore, } sf &= sg \frac{\sin \phi}{\cos \phi} = sg \tan \phi \end{aligned}$$

In like manner, for another angle of deflection  $\phi'$ , we should have  $sf' = sg \tan \phi'$ , therefore:

$$sf : sf' = \tan \phi : \tan \phi';$$

that is to say, the magnetic force of the current is proportional to the tangent of the angle of deflection.



Fig. 452.

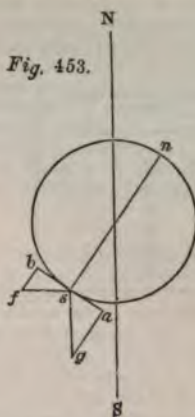


Fig. 453.

*The Sine-Galvanometer or Sine-Compass.*—To avoid any error that may arise from the different relative positions of the needle and conducting wire at different inclinations, the construction of the galvanometer is sometimes modified in such a manner as to keep the needle always in the plane of the circular conductor. For this purpose, the needle is placed in the middle of a horizontal divided circle (fig. 454), which is itself placed within a vertical circle, the two being movable together round a vertical axis, and the amount of this rotation being measured on another horizontal circle below. The conducting wire, which is of copper covered with silk, is wound several times round the vertical circle. The instrument is first placed with the vertical circle in the plane of the magnetic meridian, the magnetic needle and the index of the lower horizontal circle then standing at  $0^\circ$ . On sending the current through the wire, the needle is deflected; the vertical circle is then to be turned in the same direction, till the needle again comes into the plane of the conducting wire, and therefore to the zero of the upper horizontal circle. The amount of its deflection from the magnetic meridian is then read off on the lower circle. Since now the needle is retained in the plane of the wire, it is clear that the current acts upon it at right angles to its axis, and therefore with its full force: hence, in the position of equilibrium, this force must balance that of the earth's magnetism, which tends to bring the needle back to the magnetic meridian; but this terrestrial force varies as the sine of the angle which the needle makes with the magnetic meridian; hence also the force of the current is proportional to the sine of the angle of deflection. Hence the name of the instrument.

As the sine-compass does not require the diameter of the circle of conducting wire to be very great in proportion to the length of the needle, it is better adapted than the tangent-compass for the measurement of weak currents; but it is more complicated, and on the whole not so convenient. (For the description of a sine-compass constructed by Siemens and Halske, especially for telegraphic measurements, see Wiedemann's *Lehre vom Galvanismus und Electro-magnetismus*, ii. [1] 207.)

*Comparison between the Magnetic Galvanometer and the Voltmeter.*—By introducing into the same circuit a voltmeter and a tangent or sine-compass, it is found that the chemical action of the current is proportional to its magnetic action. The magnetic galvanometer affords therefore a measure of the chemical, as well as of the magnetic action of the current.

The indications of different tangent- or sine-compasses are not directly comparable one with the other: for, with a given strength of current, the deflection of the needle varies with the diameter of the ring, and with the intensity of the terrestrial magnetic force, so that the same instrument would give different indications in different localities. By comparison with the chemical voltmeter, however, the indications of all such instruments may be reduced to a common standard.

Fig. 454.





A series of experiments described by Müller (*Lehrbuch der Physik*, ii. 170), in which a voltmeter and a tangent-compass were included in the circuit of a Bunsen's battery, gave the following results:—

Number of cells in the battery.	Deflection of needle.	Quantity of detonating gas evolved in three minutes.
		Cubic centimetres.
12	28.5°	125
8	24.8	106
6	22.0	92.5
4	18.75	78
3	13.75	56
2	5.9	23.7

The deflection of the needle did not vary more than half a degree during the three minutes. The numbers given in the second column of the table are the mean deviations between those observed at the beginning and end of the time.

The quotient obtained by dividing the quantity of gas evolved in the minute by the tangent of the deflection, is a constant, or nearly constant quantity, which gives the volume of gas evolved in a minute by a current which would produce, with the particular tangent-compass used, a deflection of 45° (since  $\tan 45^\circ = 1$ ). The numbers in the preceding table give, for this quotient, the following values:—

No. of observation.	1	2	3	4	5	6	
Quotient	76.7	76.5	76.2	76.6	76.3	76.6	Mean 76.5

During the experiments, the temperature of the room was 15° C., the barometer stood at 744 mm., and the column of water in the voltmeter was about 10 cent. high, which is equivalent to 7 mm. of mercury. Hence the gas was under a pressure of 737 mm. Reducing by these data the mean volume of gas to 0° C. and 760 mm. pressure, the volume of gas evolved in a minute when the deflection is 45°, is found to be 70 cubic centimetres. A current which deflected the needle of the same instrument through  $\phi$  degrees, would eliminate in a minute a volume of detonating gas =  $70 \tan \phi$  cub. cent. Thus a deflection of 54° would correspond to a volume of detonating gas =  $70 \times \tan 54^\circ = 70 \times 1.376 = 96.32$  cub. cent. at 0° C. and 760 mm.

Jacobi adopts, as the unit of current strength, the current which eliminates 1 cubic centimetre of detonating gas at 0° C. and 760 mm. in a minute. If then a current which eliminates  $m$  cub. cent. of detonating gas per minute, deflects the needle of a particular tangent-compass, 45°, the strength of any other current which, with the same instrument, produces a deflection of  $\phi$  degrees, may be expressed in terms of the above unit, by the formula:

$$S = m \cdot \tan \phi.$$

The indications of the sine-compass may be compared with those of the voltmeter in a similar manner.

*Reduction of the Force of the Electric Current to absolute Mechanical Measure.*—This important determination has been made the subject of an extensive research by Weber and Kohlrausch (*Abhandlungen der math.-phys. Classe der königl.-sächsischen Gesellschaft der Wissenschaften*. Leipzig, 1856). The following are the units of measurement adopted:—

a. The unit of electric fluid is the quantity which, when concentrated in a point and acting on an equal quantity of the same fluid, also concentrated in a point, and at the unit of distance, exerts a repulsion equal to the unit of force.

b. The unit of electro-chemical intensity is the force of the current, which, in a unit of time, decomposes a unit of weight of water, or an equivalent quantity of any other electrolyte.

c. The unit of electro-magnetic force, is the force of a current which—when it traverses a circular conductor whose sectional area is equal to the unit of surface, and acts upon a magnet whose magnetic moment is equal to unity, the magnet being placed at a great distance, and in such a manner that its axis is parallel to the plane of the conductor, and its centre on a line drawn through the centre of the circular conductor, and perpendicular to its plane—exerts upon the magnet a rotatory force equal to unity divided by the cube of the distance between the centre of the needle and the centre of the conductor.

Weber had shown by previous experiments that the unit of electro-chemical force is to that of electro-magnetic force as 106 $\frac{2}{3}$  to 1. It remained, therefore, to determine the relation between the electro-magnetic unit and the electrostatic unit (1), and thus to establish a numerical relation between statical and dynamical electricity. The mode of experimenting was as follows:—



1. A Leyden jar having been strongly charged, its knob was touched with a large metallic ball, which took from it a certain portion of its charge, determined by previous experiments. The charge of the ball was then transferred to the torsion-balance, and the repulsive force measured. At the same time, the remainder of the charge of the jar was made to traverse the wire of a galvanometer, previously, however, having been passed through a long column of water, in order to give it a sensible duration, and prevent it from passing from one coil of the wire to another in the form of a spark. In this manner, a relation was established between the statical and dynamical effects of the charge of the jar.—2. The intensity and duration of a voltaic current were determined, which imparted to the galvanometer needle the same deflection as that produced by the discharge of the Leyden jar.

The results of the experiments were as follows:—

Through each section of a conductor traversed by a current whose force is equal to the electro-magnetic unit, there passes, in a second of time, a quantity of positive electricity equal to  $155,370 \times 10^6$  statical units (p. 462), an equal quantity of negative electricity travelling in the opposite direction.

The quantity of electricity required to decompose 1 milligramme of water, amounts to  $106\frac{1}{2}$  times this quantity, or  $16,573 \times 10^6$  units of electricity, of each kind. To decompose 9 milligrammes of water, or one equivalent, requires of course nine times this amount of electricity. This quantity of positive electricity ( $9 \times 16,573 \times 10^6$ ) accumulated on a cloud situated 1000 metres above the surface of the earth, and acting on an equal quantity of negative electricity on the surface of the earth below the cloud, would exert an attractive force equal to 226,800 kilogrammes, or 208 tons.

From the same data it is calculated that, if all the particles of hydrogen in 1 milligramme of water in the form of a column 1 millimetre long, were attached to a thread, and all the particles of oxygen to another thread, then, to effect the decomposition of the water in a second, the two threads would require to be drawn in opposite directions, each with a force of 147,380 kilogrammes, or 145 tons. If the water were decomposed with less velocity, the tension would be proportionally less.

#### *Electric Resistance of Conductors.*

The preceding principles enable us to determine the manner in which the resistance of a metallic wire varies with its length. For this purpose, suppose a one-celled battery (Daniell's) to be used, which maintains a constant action during the time of the experiment. First, let the current be made to pass directly through the tangent-compass, and afterwards let wires of uniform thickness and of the lengths of 5, 10, 40, 70, and 100 metres, be interposed in the circuit, and the resulting deflections observed. Now, as the force of the battery is constant, the resistance is inversely as the strength of the current. But the total resistance is made up of that of the interposed wires, together with that of the battery itself, and that of the conductor of the galvanometer. These last two resistances we may suppose to be equal to that of a wire of the same thickness as the above, and of a certain unknown length  $x$ . Instead, therefore, of the lengths of wire 5, 10, 40, &c., we must substitute  $x + 5$ ,  $x + 10$ ,  $x + 40$ , &c. An experiment of this kind \* gave the following results:—

Length of Wire.	Observed Deflection.	Tangent of Deflection.
$x$ metres	$62^\circ 0'$	1.880
$x + 5$	40 20	0.849
$x + 10$	28 30	0.543
$x + 40$	9 45	0.172
$x + 70$	6 0	0.105
$x + 100$	4 15	0.074

Now, let us assume, as most probable, that the resistance of a wire increases in direct proportion to its length, then, according to Ohm's law, the first two experiments give:—

$$x : x + 5 = 0.849 : 1.880$$

whence,  $x = 4.11$ . And, by combining in a similar manner the first experiment with all the others, we obtain for  $x$  the several values 4.06, 4.03, 4.14, 4.09, the mean of the whole being 4.08. Substituting this value for  $x$  in the preceding table, and calculating the corresponding deflections, on the supposition that the strength of the current varies inversely as the resistance, that is as the length of the conductor, we obtain the following results:—

\* Müller, *Lehrbuch der Physik*, 1853, II. 177.

Length of Conductor.	Calculated Deflection.	Observed Deflection.	Difference.
4.08 metre	62° 0'	62° 0'	
9.08	40 18	40 20	+ 2'
14.08	28 41	28 30	- 11
44.08	9 56	9 45	- 11
74.08	5 57	6 0	+ 3
104.08	4 14	4 15	+ 1

From the results of this and similar experiments, it is inferred that — *the resistance of a conductor of uniform thickness varies directly as its length.*

*The unit of resistance generally adopted is that of a wire of pure silver, 1 metre in length and 1 millimetre in diameter.* Jacobi proposed copper; but this metal is not so well adapted to the purpose as silver, on account of the difficulty of obtaining it pure.

Matthiessen has proposed for the same purpose an alloy of gold and silver, containing 2 pts. gold and 1 pt. silver, the conducting power of which he has shown to be very little affected by slight impurities in the metals, and not to be altered by annealing or by moderate variations of temperature. (Phil. Mag. [4] xxi. 107.)

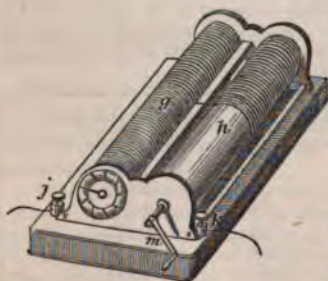
For Weber's absolute standard of electric resistance, see Pogg. Ann. lxxxii. 337; Jahresber. d. Chem. 1851, 272.

*The Rheostat or Current-regulator.*—This is an instrument for regulating and measuring the relative force of electric currents, by introducing into the circuit a conducting wire, the length of which may be varied at pleasure, without making any alteration in the rest of the circuit. This method applied to different currents, gives, as we shall see, the ratio of their intensities. The great advantage which it presents is that of bringing the indications of a galvanometer placed in the circuit, always to the same degree, by varying the resistance, and thus dispensing with the use of instruments which depend upon the relations between the deflection of the needle and the strength of the current. In fact, the mode of measurement now under consideration depends merely upon the obvious principle, that two currents of equal strength will deflect the galvanometer in the same degree.

Instruments for introducing a variable resistance into the circuit are of various construction. We shall here describe the rheostats of Professor Wheatstone, of which there are two forms, one for circuits in which the resistance is strong, the other for those in which it is weak.

The rheostat for strong resistances, (fig. 455), consists of two cylinders, *g* *h*,

Fig. 455.

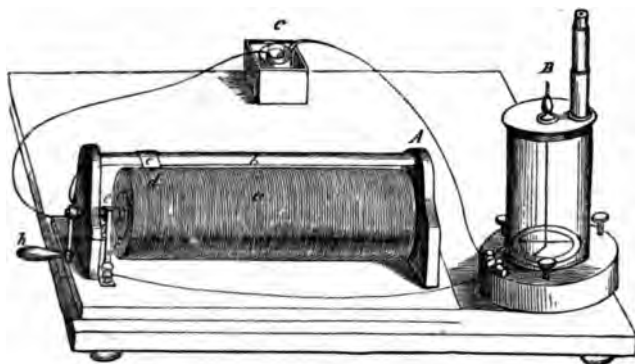


of the same dimensions, the first of dry wood, the second of brass, placed with their axes parallel to each other. The wooden cylinder *g* has a fine screw cut on its surface, and around it, following the thread of the screw, is coiled a thin brass wire. One extremity of this wire is attached to a brass ring at the nearer end of the wooden cylinder, and the other to the further extremity of the brass cylinder. The ring and the nearer end of the brass cylinder are connected with the wires of the battery, through the medium of the screw joints *j*, *k*. A movable handle *m*, serves to turn the cylinders alternately round their axes. By turning *h* to the right, the wire is uncoiled from *g*, and coiled upon *h*; and the contrary when *h* is turned to the left. The number of coils of wire upon it are indicated by a scale placed between the cylinders, the

fractions of a turn being measured by an index moving round the ring in front of the wooden cylinder, which is graduated accordingly. As the coils of the wire are insulated on the wooden cylinder, but not on the brass, it is evident that the path of the current will be longer, and therefore the resistance greater, in proportion to the number of turns which the wire makes round the wooden cylinder.

The rheostat for circuits of comparatively small resistance, is shown in figure 456; *a* is a cylinder of dry wood, having a screw cut on its surface, and a thick copper wire coiled round it in the thread of the screw. Immediately above this cylinder is a triangular bar of metal *b*, carrying a runner *c*, also of metal, to which is adapted a spring *d*, constantly pressing against the cylinder and yielding to all its inequalities. One end of the coil is attached to a brass ring *e*, against which there presses a spring communicating, by means of a binding screw, with one pole of the battery, while the other

Fig. 456.



pole is connected in a similar manner with the triangular bar. On turning the handle *A*, the cylinder revolves upon its axis, and the runner *d*, guided by the copper wire, moves along the bar in one direction or the other, according to the way in which the handle is turned. The runner is thus brought in contact with different parts of the copper wire, and a variable resistance is introduced into the circuit, according as the current has to traverse a greater or smaller length of wire between the ring *e* and the runner *c*.

The figure shows the manner of using either of these instruments. *B* is a very sensitive galvanometer, having an astatic needle, and provided with a microscope for reading off the divided circle. *C* is the battery. When the object of the experiment is to measure the resistance of a given conductor, that conductor may be introduced in any part of the circuit.

The mode of comparing the electromotive forces of two voltaic batteries is as follows:—Into the circuit of one of the batteries, a sufficient resistance is introduced by the insertion of the rheostat wire—and, if necessary, of one or more reels of wire covered with silk, to reduce the deflection of the galvanometer needle to a convenient amount, say  $45^\circ$ ,—and a further resistance, measured by a certain length of the rheostat wire, is then introduced, sufficient to bring down the deflection, say to  $40^\circ$ . Let this length be  $l$ , and let the length of wire required in like manner to reduce the deflection of the needle by the current of the second battery, also from  $45^\circ$  to  $40^\circ$ , be  $l'$ . Then the ratio of the electromotive forces of the two batteries is determined by the proportion

$$e : e' = l : l'.$$

For, using the notation explained at page 459, let the quantity of electricity which produces the deflection  $45^\circ$ , be  $q = \frac{e}{r}$ ; then the quantity  $q'$  which produces the de-

flection  $40^\circ$  is  $\frac{e}{r + l}$ . Now let the ratio of the electromotive forces of the two batteries be denoted by  $n$ , that is to say,  $e' = ne$ . Then to enable the second current to produce the same deflection,  $45^\circ$ , as the first, its resistance must also be  $nr$ ; and when the deflection is reduced to  $40^\circ$ , by the introduction of the length of the wire  $l'$ , the force of this second battery will be expressed by  $\frac{ne}{nr + l'}$ ; but this must be equal to  $\frac{e}{r + l}$ ,

which can only be the case when  $l' = nl$ ; or  $\frac{l'}{l} = n = \frac{e'}{e}$ ; that is to say, the electromotive forces are as the resistances required to reduce the deflection by the same amount in the two cases.

For example, three simple voltaic couples, differing only in the size of the plates, and each consisting of a liquid amalgam of zinc, placed in a porous cell within a vessel filled with solution of sulphate of copper, in which was also immersed a hollow cylinder of copper, were successively placed in a circuit including a rheostat. All three required the same length of wire, viz. 30 turns of the rheostat, to reduce their electromagnetic force from  $45^\circ$  to  $40^\circ$ . Nevertheless, one was 5 centimetres high and 3·8 cent. in diameter; the second 8·4 cent. high, and 3·8 cent. in diameter; and the third 15 cent. high, and 8·4 cent. in diameter. Hence the electromotive force is independent of the extent of surface in the couple.

In the compound battery, the same mode of experimenting shows that the electro-



*motive force increases proportionally to the number of plates.* Thus, in a circuit formed successively of 1, 2, 3, 4, 5 couples, similar to the smallest of those above mentioned, it was found that, to bring the deflection from  $45^\circ$  down to  $40^\circ$ , the number of turns of the rheostat wire required, were,

For 1	2	3	4	5 couples
30	61	91	120	150 turns.

Hence, excepting the cases of 2 and 3 couples, which exhibit slight variations, the proportionality between the electromotive force and the number of pairs is completely verified.

The rheostat is likewise easily applied to the measurement of the resistance offered by different conductors to the passage of the current. Suppose that when the wire of the rheostat (*fig. 455*) is completely uncoiled from the wooden cylinder (the index then standing at 0), the galvanometer shows a deflection of  $46^\circ$ . Then let a copper wire four yards long and  $\frac{1}{16}$ th of an inch thick, be introduced into any part of the same circuit. The galvanometer-needle will then exhibit a smaller deflection, say  $37^\circ$ . On removing the wire, the galvanometer will again exhibit its former deflection of  $46^\circ$ . Now let the rheostat wire be coiled round the wooden cylinder till the needle returns to  $37^\circ$ , and suppose that to produce this effect twenty turns of the rheostat-wire are necessary. This length of the rheostat wire produces a resistance equal to that of the wire under examination. Next let a similar experiment be made with a wire of the same length but of twice the thickness, and consequently having a transverse section four times as great as that of the former. It will be found that five turns of the rheostat wire, or one-fourth of the former length, are sufficient to produce a resistance equal to that of the second wire. By experiments thus conducted, it is found that: *The resistance of a wire or any other conductor of given length varies inversely as its transverse section.* And comparing this result with that which was established at page 464, we find that: *Conductors of the same material offer equal resistances, when their lengths are to one another in the same proportion as their transverse sections.*

The same law holds good for liquid conductors; hence the resistance offered by a liquid to the passage of the current may be diminished by bringing the solid conductors or electrodes, which convey the current into the liquid, more closely together, or by increasing their surface, and consequently the transverse section of the column of liquid.

The resistance of metals to the electric current increases as they become hotter; that of metalloids, acids, saline solutions, and compound bodies in general, both in the solid and in the liquid state, diminishes with rise of temperature.

The following table exhibits the comparative resistances, at ordinary temperatures, and for the same length and transverse section, of a few of the bodies commonly used in electrical experiments. These resistances are the reciprocals of the conducting powers.

Silver (chemically pure, very soft wire)	1.000
Copper	1.065
Copper, commercial (soft wire)	1.270
Brass (wire)	5.372
Iron (soft, slightly elastic wire)	6.767
Platinum wire	9.590
German silver wire	12.400
Mercury	29.238
Sulphuric acid (specific gravity 1.2 to 1.36)	761,732.000
Solution of sulphate of zinc, containing 38.58 p. c. of the crystallised salt	11,019,000.000
Solution of sulphate of copper, containing 20.83 p. c. of the crystallised salt	14,809,000.000

The resistance of distilled water is at least 700 times as great as that of dilute sulphuric acid.

The resistance of wires increases as they are harder and more brittle. (Handw. d. Chem. ii. [3] 729.)

The *conducting powers* of bodies for electricity, are, of course, inversely as their resistances. Matthiessen (Pogg. Ann. c. 178; Phil. Mag. [4] xiii. 81; Pogg. Ann. ciii. 428), has determined the conducting powers of metals, alloys, and a few other bodies, by means of an apparatus devised by Kirchhoff, and founded on the following principle, established by Wheatstone: *If four wires are joined together in a quadrangle, the ends of one diagonal being connected with a voltaic battery, and those of the other diagonal with a galvanometer, then the galvanometer will show no deflection, provided the resistances of the four wires are proportional to one another.* If then  $x$  be

the resistance of the wire to be determined,  $r$  that of a normal silver wire,  $a$  and  $b$  those of two lengths of one and the same copper wire, the unknown resistance  $x$  will, under the circumstances just mentioned, be determined by the equation  $x = r \frac{a}{b}$ .

The results obtained by this method are given in the following table:—

Conducting Powers of Metals, &c.				
Silver . . . . .	100	at 0° C.	Antimony . . . . .	4.29 at 18.7°C.
Copper* . . . . .	77.43	„ 18.8	Mercury . . . . .	1.63 „ 22.8
Gold . . . . .	55.19	„ 22.7	Bismuth . . . . .	1.19 „ 13.8
Sodium . . . . .	37.43	„ 21.8	Alloy of bismuth	
Aluminium . . . . .	33.76	„ 19.6	32 pts., anti-	0.884 „ 24.0
Zinc . . . . .	27.39	„ 17.6	mony 1 pt.	
Magnesium . . . . .	25.47	„ 17.2	Alloy of 12 bis-	
Calcium . . . . .	22.14	„ 16.8	muth + 1 tin	0.519 „ 22.0
Cadmium . . . . .	22.10	„ 18.8	Alloy of 1 zinc	
Potassium . . . . .	20.86	„ 20.4	+ 2 antimony	0.413 „ 25.0
Lithium . . . . .	19.00	„ 20.0	Graphite (greatest)	0.0893 „ 22.0
Iron . . . . .	14.44	„ 20.4	Graphite (least)	0.00395 „ 22.0
Palladium . . . . .	12.64	„ 17.2	Gas-coke . . . . .	0.0386 „ 25.0
Tin . . . . .	11.45	„ 21.0	Bunsen's bat-	
Platinum . . . . .	10.53	„ 20.7	tery-coke	0.00246 „ 26.2
Lead . . . . .	7.77	„ 17.3	Tellurium . . . . .	0.000777 „ 19.6
Nickel-silver . . . . .	7.67	„ 18.7	Red Phosphorus	0.00000123 „ 24.0
Strontium . . . . .	6.71	„ 20.0		

More extended tables of the conducting powers of metals and alloys are given in Wiedemann's *Lehre vom Galvanismus und Electromagnetismus*, i. 180. See also the article METALS, in this Dictionary.

Matthiessen has also shown (Proc. Roy. Soc. i. 516) that all pure metals in the solid state vary in conducting power to the same extent between 0° and 100° C.; but that the conducting power of a metal does not vary in the exact inverse ratio of the temperature, as stated by Becquerel and others; the resistance,  $\lambda$ , of a metal at the temperature  $t$  degrees being, in fact, expressed by the equation:

$$\lambda = x + yt + \gamma t^2;$$

where  $x$  is the resistance at 0° and  $y$  and  $\gamma$  are constants.

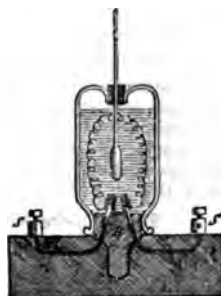
#### HEATING EFFECTS OF THE ELECTRIC CURRENT.

The continuous, as well as the sudden discharge of electricity, raises the temperature of the conductors through which it passes; the plates and liquids of the battery, as well as the connecting wires which close the circuit, and the electrolytes which are decomposed by the current, all become heated in various degrees, according to their specific heats and the resistance which they offer to the passage of the current.

The laws of the development of heat by the electric current have been examined chiefly by Lenz and Joule, who have arrived at nearly the same results. Lenz made use of the apparatus represented in *fig. 457*. A glass stopper  $b$  fixed in a board, is fitted by grinding into the mouth of a bottle, and made air and water-tight by means of a little grease. A brass clamp, not shown in the figure, serves to press the horizontal lip of the bottle tight against the board, so that it cannot be disturbed, even by violent agitation of the apparatus. At the top of the bottle, there is an aperture for pouring in liquid and fixing a thermometer by means of a cork. The stopper  $b$  is pierced with two holes, through which are inserted thick platinum wires connected by copper wires with the binding screws  $f$   $s$ , and thence with the poles of a voltaic battery. The ends of these wires within the bottle are connected by a thin platinum wire wound into a spiral. The vessel is nearly filled with a measured quantity of alcohol of 85 or 86 per cent.; water would conduct too well, and suffer decomposition to a slight extent, yielding small quantities of gas. A tangent-compass and a rheostat are introduced into the circuit, in order to measure and regulate the strength of the current.

The following table gives the results of sixteen experiments made with three wires of German silver of different thicknesses, and with wires of platinum, iron, and copper.

*Fig. 457.*



\* See the article COPPER, p. 29 of this volume.

The resistance of the spiral wire was determined by removing the apparatus from the circuit, and ascertaining the number of turns of the rheostat-wire required to be brought into the circuit to bring the current to the same strength. These resistances and the strength of the current, in the second column, are expressed in Jacobi's units already mentioned (pp. 462, 464):—

No. of experiment.	Nature of the wire.	Strength of current.	Time required to heat the spirit 1° R.	Resistance of the wire.
1	Nickel silver, <i>a</i> . . .	6·93	1·349	93·60
2	" " . . .	10·53	0·571	93·63
3	" " . . .	14·30	0·300	58·76
4	Nickel-silver, <i>b</i> . . .	10·53	0·920	58·64
5	" " . . .	14·30	0·481	59·01
6	" " . . .	18·32	0·288	60·16
7	" " . . .	14·30	0·457	44·59
8	Nickel-silver, <i>c</i> . . .	18·32	0·384	50·45
9	Platinum . . .	22·69	0·555	51·41
10	" . . .	18·32	0·325	24·92
11	Iron . . .	22·69	0·435	13·90
12	Copper . . .	18·32	1·301	13·90
13	" . . .	22·69	0·835	13·90
14	" . . .	27·52	0·675	13·92
15	" . . .	32·98	0·381	14·01
16	" . . .	27·52	0·544	14·31

The quantity of spirit in the bottle was 90 grammes.

Comparing now with one another the experiments in which the strength of the current was the same, it appears that the product of the time  $t$  and the resistance  $l$  is a constant quantity. Thus:

For the current 10·53.

2. Nickel-silver, *a* . . . . .  $tl = 53·46$   
 4. " " *b* . . . . .  $tl = 64·06$

For the current 14·30.

3. Nickel-silver, *a* . . . . .  $tl = 28·18$   
 5. " " *b* . . . . .  $tl = 28·11$   
 7. " " *c* . . . . .  $tl = 27·49$   
 9. Platinum . . . . .  $tl = 28·00$

For the current 18·32.

6. Nickel-silver, *b* . . . . .  $tl = 16·99$   
 8. " " *c* . . . . .  $tl = 17·12$   
 10. Platinum . . . . .  $tl = 16·71$   
 12. Copper . . . . .  $tl = 18·08$

For the current 22·69.

11. Iron . . . . .  $tl = 10·84$   
 13. Copper . . . . .  $tl = 11·60$

These numbers show that, with a given strength of current, the time of heating is inversely proportional to the resistance, or the heat evolved in a given time is directly proportional to the resistance, and otherwise independent of the nature of the metal.

Secondly, by comparing together the experiments made with the same wire and currents of different strengths ( $s$ ), it will be found that the product  $s^2t$  is nearly constant, thus:

For the nickel-silver wire *a*.

- 1 . . . . .  $s^2t = 64·8$   
 2 . . . . .  $s^2t = 63·3$   
 3 . . . . .  $s^2t = 61·3$

For the nickel-silver wire *b*.

- 4 . . . . .  $s^2t = 102·0$   
 5 . . . . .  $s^2t = 98·4$   
 6 . . . . .  $s^2t = 96·7$   
 7 . . . . .  $s^2t = 93·5$

For the platinum wire.

- 9 . . . . .  $s^2t = 113·5$   
 10 . . . . .  $s^2t = 109·1$

For the copper wire.

- 12 . . . . .  $s^2t = 436·6$   
 13 . . . . .  $s^2t = 429·9$   
 14 . . . . .  $s^2t = 435·5$   
 15 . . . . .  $s^2t = 414·2$   
 16 . . . . .  $s^2t = 412·0$



It appears then from these experiments, that *the evolution of heat is proportional:*  
 1. *To the resistance;* 2. *To the square of the strength of the current.*

These laws are the same as those demonstrated by Riess for the heating of wires by the sudden discharge of electricity (p. 395).

Further, as  $t$  is the time in which, with the current  $s$  and the resistance  $l$ , a given mass of alcohol is heated  $1^\circ$  Réaumur,  $s^2t$  will be the time required for heating the same mass of alcohol  $1^\circ$  R. by the unit of current force acting against the unit of resistance. Since, therefore, in all the preceding experiments, the quantity of alcohol was nearly the same, the product  $s^2t$  ought to be nearly constant for all the numbers in the preceding table, as in fact it is, the greatest and least values, being 6609 and 6069, and the mean 5856.

Now, the quantity of alcohol heated in the preceding experiments, together with that which would be equivalent (as regards specific heat) to the mass of glass heated at the same time, was 118 grammes. Hence the unit of current force passing through a wire, whose resistance is  $l$ , evolves heat sufficient to raise the temperature of 118 grammes of the alcohol used,  $1^\circ$  R. in 5856 minutes.

The specific heat of the alcohol (85 to 86 per cent.) is 0.7, so that 118 grammes of this alcohol require, to heat it through a given range of temperature, as much heat as  $118 \times 0.7 = 82.6$  grammes water. Consequently, the time required to heat 1 gramme of water  $1^\circ$  R. by the unit of current force acting with the unit of resistance is:

$$\frac{5856}{82.6} = 70.9 \text{ minutes;}$$

and for  $1^\circ$  Centigrade the time is:

$$70.9 \times 0.8 = 56.72 \text{ minutes;}$$

that is to say: *When a current of the unit of strength passes through a wire whose resistance is equal to that of a copper wire 1 metre long and 1 millimetre in diameter, it develops a quantity of heat sufficient to raise the temperature of 1 gramme of water,  $1^\circ$  C. in 56.72 minutes; and assuming as the unit of heat the quantity required to raise the temperature of 1 gramme of water  $1^\circ$  C., the result of the preceding experiments may be thus expressed:*

*A current of the unit of strength, passing through a conductor which exerts the unit of resistance, develops therein 1.057 heat-units in an hour, and 0.0176 heat-units in a minute.*

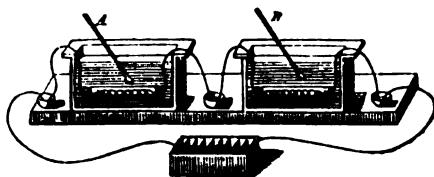
As the temperature of a metallic conductor rises under the influence of the electric current, its resistance to the passage of the current increases (p. 466). Now this increase of resistance acts in two ways: first, by diminishing the strength of the current; secondly, by increasing the heating effect of the electricity which actually passes, so that ultimately these effects balance one another. From the experiments of Robinson (*Trans. of the Royal Irish Academy*, xxii. [1] 8), it appears that the resistance gradually increases up to the melting-point of the wire, the increase being very nearly proportional to the temperature.

The effect of temperature on conducting power is strikingly shown by heating a long platinum wire to low redness by the current, and then plunging the middle part of it into cold water; the extremities immediately become brightly incandescent. On the contrary, if one part of the wire be raised to a very high temperature by means of a spirit-lamp or blowpipe flame, the glow of the other part immediately diminishes in brightness.

The heating of wires by the current is remarkably affected also by the cooling action of the surrounding gaseous medium. A platinum wire is heated to redness much more easily in a vacuum than in air, and more easily in some gases than in others, hydrogen exerting the greatest cooling effect, and nitrogen the least. But further, this abstraction of heat from the wire by a gas, not only lowers its actual temperature, but at the same time diminishes the resistance which it offers to the passage of the current, and therefore also the quantity of heat actually developed in it. This is strikingly shown by the following experiments of Grove.

Two glass tubes (fig. 458) closed at both ends with corks, and having spirals of platinum wire within them attached to thick copper wires passing through the corks,

Fig. 458.



are filled, one with hydrogen, the other with oxygen, and immersed in glass troughs containing equal quantities of water, thermometers *A, B*, being immersed in the water to measure the temperature. On sending the current of an eight-pair Grove's battery through the wires, that in the oxygen-tube is heated to whiteness, while the one in the hydrogen-tube scarcely exhibits a visible glow. Moreover, the temperature of the water in the two vessels rises very unequally; that which contains the oxygen-tube rising from  $15.5^{\circ}$  to  $27.2^{\circ}$  C. while that which contains the hydrogen-tube rises only from  $15.5^{\circ}$  to  $21^{\circ}$ . The following table shows the rise of temperature produced in the water when the platinum-wire is surrounded with different gases, associated in each case with a similar platinum wire surrounded with hydrogen:—

Hydrogen . . . . .	5.5°
Sulphydric acid . . . . .	6.0
Ethylene . . . . .	9.2
Carbonic anhydride . . . . .	11.0
Carbonic oxide . . . . .	11.0
Oxygen . . . . .	11.7
Nitrogen . . . . .	12.0

That the differences are really due to the increased conducting power of the wire resulting from the cooling, is shown by placing a voltameter in the same circuit with a platinum wire immersed successively in each gas. The following table gives the results obtained by Grove:—

Gas surrounding the wire.	Quantity of detonating gas evolved per minute.
Hydrogen . . . . .	138.6
Ethylene . . . . .	126.0
Carbonic anhydride . . . . .	118.8
Carbonic oxide . . . . .	118.8
Oxygen . . . . .	117.0
Nitrogen . . . . .	115.0

The order of the gases in this table is the same as in the preceding.

The development of heat in liquids by the electric current is regulated by the same laws as in metals, the quantity of heat evolved in a given time being proportional to the resistance of the liquid, and to the square of the strength of the current (E. Becquerel, *Ann. Ch. Phys.* [3] ix. 21). Moreover, Joule has shown (*Phil. Mag.* [3] xix. 210) that the evolution of heat in each couple of the voltaic battery is subject to the same law, which therefore holds good in every part of the circuit, and therefore also for the entire circuit, including the battery.

With a current of given strength, the sum of the quantities of heat evolved in the battery, and in the metallic conductor joining its poles, is constant, the heat actually developed in the one part or the other, varying according to the thickness of the metallic conductor. This was first shown by De la Rive, and has been confirmed by Favre (*Ann. Ch. Phys.* [3] xl. 393). De la Rive made use of a couple consisting of platinum and distilled zinc, or cadmium, excited by pure and very strong nitric acid, the two metals being united by a platinum wire, more or less thick, which was plunged into the same quantity of strong nitric acid contained in a capsule similar to that which held the voltaic couple. By observing the temperatures in the two vessels by delicate thermometers, the sum of these temperatures was found to be constant, the one or the other being greater, according to the thickness of the connecting wire.

Favre, by means of a calorimeter, similar to that which he used in his experiments on the development of heat by chemical action (see HEAT), has shown that, in a couple consisting of zinc and platinum, excited by dilute sulphuric acid and connected by platinum wires of various length and thickness, for every 33 grammes of zinc dissolved, a quantity of heat is developed in the entire circuit, equal to 18,137 heat-units (the unit of heat being the quantity required to raise 1 gramme of water from  $0^{\circ}$  to  $1^{\circ}$  C.), but variously distributed between the battery-cell and the wire, according to the thickness of the latter. Now this quantity of heat is nearly the same as that which is evolved in the simple solution of 33 grammes of zinc in dilute sulphuric acid, without the formation of a voltaic circuit, viz. 18,444 units. Hence Favre concludes that the heat developed by the resistance of a metallic or other conductor connecting the poles of the battery is simply borrowed from the total quantity of heat evolved by the chemical action taking place in the battery, and is rigorously complementary to that which remains in the cells of the battery, the heat evolved in the entire circuit being the exact equivalent of the chemical action which takes place. If any external work is performed by the current, such as electrolysis or mechanical work, as by an electromagnetic engine,

the heat evolved in the circuit is diminished by the heat-equivalent of the decomposition or mechanical work done. (Favre, *Compt. rend.* xlv. 56.)

#### LIGHT PRODUCED BY THE ELECTRIC CURRENT.

The closing and interruption of the voltaic circuit are attended with the production of sparks. With a single pair of plates, however, the spark, unless assisted by the formation of induced currents (p. 462), or by the combustion of the metallic surfaces between which it passes, is scarcely perceptible. Thus, when two short wires attached to the plates of a single voltaic couple are brought together, only a very faint spark is produced, either on making or on breaking contact; but if the same plates are connected by a long copper wire formed into spiral, the spark is much brighter, especially on breaking contact, because the induced current then coincides in direction with the primary current. A still higher exaltation of the effect is produced on placing a bar of iron within the coil. When a cup containing mercury is fixed on one of the plates, and a wire attached to the other is brought down to the surface, a bright spark is produced, the light being probably intensified by the combustion of the mercury.

A compound battery of four or more couples gives a spark between the connecting wires without any of the means of assistance just mentioned; but, unless the number of plates is very large indeed, the spark does not strike through a perceptible distance like that of the electrical machine or the induction coil. Jacobi found that the poles of a 12-pair Grove's battery did not give a spark, even at the distance of 0.00005 of an inch. Gassiot's water-battery of 3520 pairs well insulated (p. 422), gave sparks when the distance between its polar wires was reduced to 0.02 inch, the spark discharge going on without interruption for five weeks. In all ordinary cases, the light of the spark produced by the battery appears to arise in great part from ignition, fusion, or combustion of the metallic surfaces.

The most brilliant manifestation of voltaic light is that which is produced when the discharge takes place between two pointed pieces of charcoal. The light is white and dazzling, and when produced by a powerful current, such as that of a Bunsen's battery of 40 or 50 cells, has a brilliancy which the eye cannot endure. With such a battery, the charcoal points, after having been brought in contact, may be separated to some distance from one another without interrupting the current, the discharge then assuming the form of a splendid arch of light. This phenomenon takes place in a vacuum as well as in air, and even with greater regularity in the former case, because the extremities of the charcoal terminals do not then burn away.

The light of the voltaic arc is due, partly to the electric light itself, partly to the incandescence of the charcoal terminals, partly to the transport of small particles of carbon from the positive to the negative pole. By projecting the image of the poles during the passage of the current, on a screen by means of a system of lenses, this transference of particles may be distinctly seen, the positive terminal being gradually eaten away, while the negative terminal seems to grow. With the softer kinds of charcoal this transference takes place more easily than with hard charcoal; soft charcoal gives therefore a longer arc; hard charcoal is, however, usually preferred for producing the light, because the continual alteration in the terminals interferes greatly with the steadiness of the light.

The transference of matter takes place between metal terminals as well as with charcoal, the more fusible or oxidable metals, zinc and iron for example, exhibiting it more easily than the more refractory or less oxidable, such as platinum or silver; hence the arc may also be produced with metals, but it is then much shorter. In almost all cases, the transference of matter is from the positive to the negative pole, and when the discharge takes place between oxidable metals in the air, the transferred matter always consists of the oxidised metal of the positive terminal. The same transference of matter takes in the ordinary electric spark, as observed long ago by Fusinieri.

The intensity of the light of the voltaic arc has been examined by Casselmann (*Pogg. Ann.* lxxiii. 576). The charcoal terminals were formed of hard Bunsen's charcoal (i. 760) saturated with various solutions, nitrate of strontium, boric acid, &c., and then re-ignited. The terminals thus prepared gave a very steady arch of light, variously coloured, according to the substance with which the charcoal was impregnated, and continuing (with a battery of 44 Bunsen's cells) till the points were separated by an interval of 7 or 8 mm., whereas the unsteady arc produced with crude charcoal did not pass over a space exceeding 5 mm.

The following table exhibits the intensity of light of the glowing charcoal points, together with that of the luminous arch, compared with that of a stearine candle, and in each instance, when the terminals were very close, and when they were separated as far as possible. The strength of the current, measured by a tangent-compass, is expressed in chemical units (p. 462). The light was measured by a Bunsen's photometer:—



	Distance between charcoal points.	Strength of current.	Intensity of light.
Crude charcoal . . . . .	0.5 mm.	95	932
	4.5	68	139
Charcoal with nitrate of strontium .	0.5	120	353
	6.75	88	274
Charcoal with caustic potash . .	2.5	101	150
	8.0	82	75
Charcoal with chloride of zinc .	1.0	80	624
	5.0	67	159
Charcoal with borax and sulphuric acid . . . . .	1.5	72	1171
	5.0	64	165

These numbers show that both the strength of the current and the intensity of the light diminish as the distance between the terminals is increased.

From the experiments of Fizeau and Foucault, it appears that the intensity of the voltaic arc of a 46-pair Bunsen's battery is thirty-four times as great as that of the oxy-hydrogen lime-light.

The great intensity of the voltaic light has led to various attempts to adapt it to the purposes of illumination. There is, however, considerable difficulty in obtaining a steady light, because, as already observed, the charcoal terminals are continually burning away, and their shape is constantly varying, in consequence of the transference of particles from one to the other. Unless, therefore, some means are provided for maintaining a constant distance between them, the light continually varies in intensity, and sometimes goes out altogether. The most effectual arrangement for this purpose is that adopted by Duboscq in his electric lamp, for a description and figure of which, see *De la Rive's Traité*, ii. 26, or *Ure's Dictionary of Arts, Manufactures, and Mines*, ii. 87. This apparatus is admirably adapted for optical purposes, for exhibiting effects of refraction, dispersion, polarisation, &c., for throwing images of various objects on a screen, and for certain theatrical effects where a strong beam of light is required; but for general purposes of illumination, where a number of small lights are required, rather than one very strong light, the electric light does not appear to be very well adapted, because every break in the circuit increases enormously the battery power required to overcome the resistance.

Mr. Way has obtained a very bright light by passing the electric current along a stream of mercury. The light is produced by the incandescence of the mercury vapour; it has a somewhat flickering character, and a decided greenish tinge.

The magneto-electric light has also been applied to the purpose of illumination, a number of soft iron keepers carrying coils of wire being made to revolve, by steam power, in front of a series of magnetic poles. An apparatus of this kind was tried at the South Foreland Lighthouse for a year, with very good results, as regards the intensity and steadiness of the light.

The stratification of the electric light in highly-rarefied gases has been already mentioned (p. 391). This phenomenon, first observed with the discharge of the induction-coil, has been shown by Mr. Gassiot to be likewise produced by the discharge from the conductor of an electrical machine or from a Leyden jar, and by that of a voltaic battery consisting of a large number of cells, such as Gassiot's water battery, or a Grove's battery of 400 cells well insulated, so as to obtain high tension at the poles. It is therefore wholly independent of the peculiar conditions of the induction apparatus. In short, the stratifications are produced, whether the discharge is continuous, like that of the voltaic battery under ordinary circumstances, or intermittent like that of the water battery, or that of the nitric acid battery just mentioned, when a small interruption is made in the circuit, so as to give rise to the passage of sparks; but they are much more brilliant with the (apparently) continuous than with the intermittent discharge, because the action of the battery is much more energetic in the former case. Mr. Gassiot regards the stratified discharge as arising, in all cases, from the impulses of a force acting on highly-attenuated but resisting media, and thence concludes that the discharge of the voltaic battery, under every condition, is not continuous but intermittent, consisting of a series of pulsations or vibrations of greater or less velocity, according to the resistance in the metallic and electrolytic elements of the battery, and the conducting media through which the discharge passes. (*Proc. Roy. Soc.* x. 393; xii. 529.)

The voltaic arc and the streams of electric light produced in rarefied gases, are deflected by the magnet, like a wire conveying a current of electricity. Some very

remarkable phenomena are exhibited when the pole of a magnet is held near the metallic terminals in an exhausted tube through which the discharge is passing, the current being sometimes completely interrupted, as if the luminous stream had been driven away from the terminal, and thus the continuity of the circuit broken. (Proc. Roy. Soc. ix. 146, 604; x. 269.)

#### PHYSIOLOGICAL ACTION OF THE ELECTRIC CURRENT: ANIMAL ELECTRICITY.

*General Law of Nervous Excitation by the Electric Current.*—A voltaic battery of a moderate number of pairs, gives a shock at the moment when the circuit is completed by touching the two poles with the hands, and likewise on interrupting the circuit; but the continuous passage of a current of constant strength does not produce any nervous agitation.

For more delicate observations on the physiological action of electricity, the limbs of a recently killed frog are used, prepared as in Galvani's original experiment (p. 415), by cutting through the spinal column, leaving three or four vertebrae, then stripping off the skin, and leaving the lower extremities suspended by the lumbar nerves, as in fig. 459. Sometimes only one of the legs is used, with a considerable length of the lumbar nerve attached to it, and without the vertebrae. Such a preparation, which gives exceedingly delicate indications of the presence of an electric current, is called a galvanoscopic or rheoscopic limb.

In the rheoscopic limb, as in the human body, the contractions are produced at the closing and opening of the circuit, or generally on the occurrence of any variation in the strength of the current, but not while it continues of constant strength. In this respect the physiological action of the current resembles its inductive action (p. 451). The nervous agitation produced by a current of given strength is greater in proportion as the variations in its strength take place more quickly; hence the discharge of a Leyden jar, even if of small dimensions, produces a very violent shock, the current, though very small in quantity, passing through all its variations, from the commencement to its maximum strength, and down again to its termination, in a time inappreciably small.

The preceding observations must, however, be understood as applying only to the action of the current on the motor nerves; for the nerves of sensation are affected by the continuous current, as well as by the sudden discharge; a peculiar sensation is experienced when the current of a voltaic battery of a considerable number of pairs is

Fig. 459.

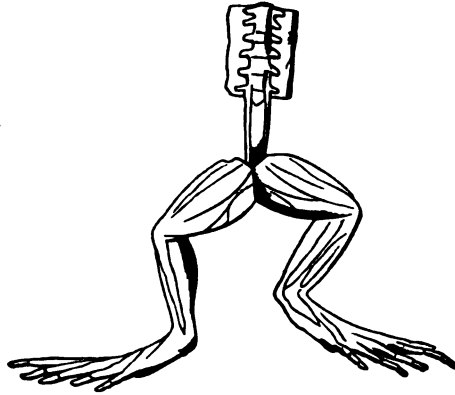
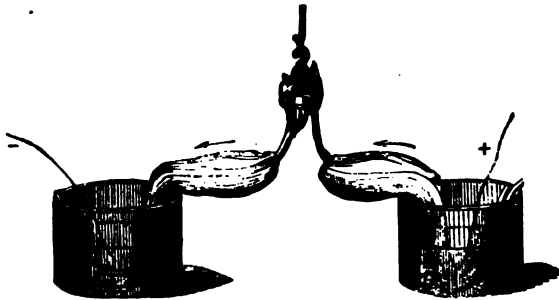


Fig. 460.



passed through any part of the body, and the current, even of a single pair, produces a severe sensation of smarting when it passes over any part of the surface from which the skin is abraded. The effect on the nerves of sensation, like that on the nerves of



motion, is, however, much greater at the commencement and cessation of the current than during its continuance.

Recently-prepared frog's legs, which are very excitable, exhibit equally strong convulsions, both at the opening and closing of the circuit, in whichever direction the current is sent through them; but as the excitability becomes less, this equality no longer exists, and Du Bois-Reymond has shown, that, with a medium degree of excitability in the prepared frog's limb, the contractions are stronger at the closing of the circuit, when the positive current passes from the origin of the nerves to their ramifications, and at the opening of the circuit, when the current is in the contrary direction. This may be shown by immersing the two legs of the frog in separate glasses of salt water connected with the poles of a battery, as in *fig. 460*, so that the  $+E$  may pass up one leg and down the other; it will then be found that the leg in the cup connected with the negative pole exhibits convulsions at the closing of the circuit and the other at the opening.

**The Muscular Current.** The rheoscopic limb may be made to exhibit convulsions without the action of any external source of electricity. Galvani, who first observed the contractions produced on touching the nerves of the limb with a copper, and the muscles with an iron rod, the two metals being in contact, attributed the effect to a peculiar fluid which he supposed to pass through the limb from the nerves to the muscles. Volta, however, showed that an essential condition to the production of the powerful contractions observed by Galvani, was the presence of two metals in the circuit, and he attributed the entire effect to electricity developed at the point of contact of the dissimilar metals (p. 415). The invention of the pile, to which this theory led him, and the splendid series of discoveries thence resulting, diverted attention for a considerable time from the original phenomenon. Galvani, however, retained his original view, and succeeded in showing, that the prepared frog's limbs, when very excitable, that is to say, soon after separation from the living body, exhibit the contractions, not only when the nerves and muscles are connected by a homogeneous metallic wire, but even without any metal at all, namely, by simply bringing the extremities of the lumbar nerves in contact with the muscles of the leg or foot.

The contractions may also be produced by dipping the feet into a vessel containing salt water, the vertebral column into another vessel of salt water placed by the side of it, and connecting the two portions of liquid by means of a bundle of moistened cotton threads; the limbs exhibit convulsions every time the circuit is completed or broken.

If the two vessels are connected by dipping into them platinum plates attached to the coil of a very delicate galvanometer, the needle exhibits a deflection, indicating the existence of a current from the feet towards the head. This was first shown by Nobili; and Matteucci afterwards found that an equally strong current is produced, when, instead of the prepared limbs, the entire body of a frog, recently killed and skinned, is placed between the two glasses, with the head in one and the feet in the other, the current always passing in the body of the frog from the feet to the head. With the galvanoscopic limb, a current is obtained still in the same direction, when the leg is immersed in one vessel and the thigh in the other.

As the saline solutions may act chemically on the animal fluids, and thus generate currents which interfere with the true muscular and nervous currents, it is necessary, in the more delicate investigations relating to animal electricity, to make use of apparatus in which the direct contact of the nerves

and muscles with these solutions is avoided. Such is the contrivance adopted by Du Bois-Reymond (*Untersuchungen über thierische Electricität*, Berlin, 1848 and 1849; *Ann. Ch. Phys.* [3] xxx. 119, 178; xxxix. 114), which consists in laying the nerve or muscle between two pads, composed of a great number of layers of thin filtering paper, saturated with the saline solution, and laid over the edges of the vessels in which the platinum terminals of the galvanometer are immersed, the animal substance not, however, being in direct contact with the moistened paper, but separated from it by a

*Fig. 461.*



small piece of moistened bladder soaked in white of egg: this prevents any chemical action between the saline solution and the animal fluids, but does not stop the current.

During the intervals between the experiments, the two pads are connected by a third, as shown in the figure, the object of this connection being to keep the circuit closed, and allow any polarisation of the platinum plates that may have taken place to neutralise itself.

A better mode of experimenting, however, is that of Matteucci (*Proc. Roy. Soc.*



x. 577), who uses, as extremities of the galvanometer, plates of amalgamated zinc, immersed in a neutral saturated solution of sulphate of zinc. This liquid possesses great conducting power, but does not act chemically on the animal tissue; the apparatus is also quite free from secondary polarity.

By the mode of experimenting above described, the following facts have been established:—

1. When a muscle having two membranous terminations is laid between the conducting pads, as in *fig. 462*, no current is produced; but if the muscle is placed as in

*Fig. 462.*



*Fig. 463.*



*fig. 463*, with one of its extremities in contact with one pad, and its red muscular surface with the other, a very strong current is produced, passing through the muscle from the tendinous extremity, *a*, to the point of contact of the muscular flesh with the pad. If the muscle be removed, the circuit completed by the connecting pad, so as to destroy the polarity of the plates, the connecting pad then removed, and the position

*Fig. 464.*



*Fig. 465.*



of the muscle reversed as in *fig. 464*, the direction of the current is reversed, that is to say, it is still from the tendinous extremity *b*, to the touched point of the muscular flesh.

2. If the muscle be cut transversely and then placed between the pads, so that the cut surface, *a*, is in contact with one, and a point of the outer surface with the other (*fig. 465*), the current passes from *a* through the muscle towards the latter point.

The artificial transverse section of the muscle plays, therefore, the same part as the tendinous extremity; in fact, this extremity may be regarded as a natural transverse section, covered with a neutral substance, the tendon, which acts merely as a conductor.

3. If the muscle be torn in the direction of the fibres, an artificial longitudinal section is obtained, which acts just like the natural lateral surface of the muscles, or natural longitudinal section.

These results lead to the following general law of the direction of the muscular current,

*The longitudinal section, natural or artificial, of a muscle, is positive to its natural or artificial transverse section.*

This law of the muscular current is not confined to any particular class of animals, but extends throughout the animal kingdom. Du Bois-Reymond has observed it in the muscles of man, of the rabbit, guinea-pig, mouse, dove, sparrow, tortoise, lizard, adder, blind-worm, many kinds of frog and toad, the earth- and water-salamander, the river-crab, and the common earth-worm.

Du Bois-Reymond has further shown that currents exist between different points of the longitudinal section, either natural or artificial, any point in such longitudinal section being negative with respect to any other point farther than itself from the extremity of the section.

The central points of any transverse section are negative to those situated beyond them.

These currents existing between different points of the same section, longitudinal or transverse, are, however, very feeble in comparison with those between a transverse and a longitudinal section.

It appears, then, that every fragment of a muscle, however small, exhibits currents following the same general law. Hence it may be inferred that the muscular currents are *molecular*, like those to which the effects of magnetism are attributed in Ampère's theory, so that the muscular currents really form closed circuits, and the currents actually observed in experiments like those above described, are merely derived currents,

obtained by diverting a portion of the principal current through a neighbouring conductor, and probably very greatly inferior in intensity to the primitive currents.

The strength of the muscular current is greater in proportion as the muscle has to exert a stronger mechanical power, whether voluntary or involuntary (Du Bois-Reymond). According to Matteucci (Proc. Roy. Soc. viii. 209), the electromotive power of a muscle is independent of the surface of its transverse section, but increases with the length of the muscle. It is greater in mammals and birds than in fish or amphibia.

The nerves have no direct influence on the electromotive force of muscles, but any causes which exert an influence on the physical structure and chemical composition of muscles, so as to modify their irritability or contractility, act equally on their electromotive power. (Matteucci, *loc. cit.*)

According to J. Regnaud, the maximum electromotive force of the gastro-cnemian muscle of the frog is between 4 and 5 times as great as that of a thermo-electric couple of bismuth and antimony having one of its joints at 0° C. the other at 100°; that of the thigh-muscles of the frog is 9 or 10 times that of the same couple. Referred to the same unit, the electromotive force of the gastro-cnemius of the rabbit is between 6 and 7, that of the biceps between 5 and 6.

The electromotive power of the muscles diminishes after death at the same rate as the irritability, and when the rigidity of death sets in, the muscular current ceases altogether, and cannot be renewed by any means whatever. It is therefore essentially a vital phenomenon.

A muscle during contraction exhibits an electric current in the same direction as when it is in the uncontracted state, but the current is much weaker. (Du Bois-Reymond, Matteucci.)

**The Nervous Current.** By operating with the sciatic nerve of a frog in the same manner as in the experiments with muscle above described, placing a transverse section in contact with one of the pads of filtering paper, and a point of the lateral surface with the other, a strong current is obtained, passing from the transverse section through the nerve to the touched point of the lateral surface.

Generally, the nervous current is subject to the same laws as the muscular current; the nerves may therefore be supposed to be the seat of a number of closed molecular currents, of which the currents actually indicated by the multiplier are merely derived portions, greatly inferior in strength to the nervous currents themselves.

When an electric current from a voltaic couple is passed along any portion of a nerve, the nerve begins to act electromotively at all its points, independently of its ordinary electric state, the direction of the currents thus produced coinciding with that of the exciting current. This is called the electro-tonic state of the nerve.

When, on the contrary, the nerve is tetanised, by the passage of momentary currents through it in opposite directions, as from an induction-coil, the ordinary nervous current is weakened, like the muscular current under similar circumstances.

For further details on the muscular and nervous currents, see Müller *Lehrbuch der Physik*, ii. 410-432.—De la Rive, *Traité* iii. 1-61.—Matteucci, *Ann. Ch. Phys.* [2] lvi. 429; lxxviii. 93, [3] vi. 30; viii. 309; xv. 64; xviii. 109; xxiii. 230; *Phil. Trans.* 1847-1850;—Proc. Roy. Soc. viii. 209; x. 344.—C. B. Radeliffe, *ibid.* ix. 690; x. 347.

**Electric Fishes.** There are certain fishes provided with peculiar organs, in which electricity is developed with such intensity as to give powerful shocks, and exhibit various other signs of electric action, such as attraction and repulsion, the spark, magnetisation of steel, &c.

The fishes in which this power is known to reside, are the *Torpedo* or *Electric Ray*, found in the Mediterranean and in the Atlantic, rarely in the North Sea; the *Gymnotus electricus* or *Surinam El*, found in the lakes and rivers of South America, especially in Guiana; and the *Silurus electricus*, found in the Nile, Niger, and other African rivers. Besides these, the *Rhinobatus electricus*, *Tetraodon electricus*, and *Trichiurus electricus*, are said to possess similar powers, but the statements respecting them are somewhat vague and require confirmation.

The torpedo has long been known to possess the power of giving shocks; but the electric character of this power was first pointed out by Muschenbroek, and further established by Dr. John Davy, who obtained a deflection of a galvanometer needle by bringing the extremities of the coil, furnished with platinum plates, in contact with the back and front of the fish, and magnetised a steel needle by placing it in a helix, the ends of which were made to touch the fish in a similar manner. He likewise succeeded in decomposing water by the same current, and proved, by the manner in which this decomposition took place, as well as by the magnetic phenomena, that the upper or back surface of the torpedo is positive, the lower negative. These results

were confirmed by Becquerel and Breschet, and further by Matteucci and Linari. The latter first obtained a spark from the torpedo by bringing an iron wire touching one surface of the fish in contact with a cup of mercury connected with the opposite surface; he likewise obtained an induction-spark by passing the discharge from the fish through an electro-dynamic helix. Matteucci afterwards obtained a spark and effects of attraction, by placing a torpedo just taken out of the water between two metallic plates (*fig. 466*), the lower supported on glass legs, the upper provided with an insulating handle, and both having attached to them metallic rods, terminating in balls *A B*, to which gold leaves were attached. On gently moving the upper plate, so as to irritate the animal a little, the gold leaves moved together, and a bright spark passed between them.

In the gymnotus, the direction of the electric discharge is from the head through an external conductor to the tail, the head being the positive extremity. When the fish bends its long body into a curve, the water included in the curve is traversed by a number of electric currents, which kill any small fishes that may be in their way. Faraday showed that the electric current from the gymnotus is capable of decomposing iodide of potassium, magnetising steel needles, and producing an induction spark; and Schönbein, by connecting two strips of gold leaf, one with the head, the other with the tail of the fish, obtained vivid sparks, attended with combustion of the gold.

The shock given by the gymnotus is much more powerful than that of the torpedo; indeed, when the fish is in full vigour in its native element, it is capable of killing large animals. The discharge from both these fishes is of high intensity, like that of a Leyden jar, and will give a shock to a chain of several persons joining hands.

The power of all the electrical fishes resides in peculiar organs, bearing a general resemblance to a voltaic pile. In the torpedo, the electrical organ, situated between the pectoral fins, the head, and the gills, is formed of a number of small membranous tubes, *A, B* (*fig. 467*), passing perpendicularly from front to back of the fish, pressed together like the cells of a honey-comb, and divided by transverse diaphragms into a great number of small cells, which are filled with an albuminous liquid ( $\frac{9}{10}$  salt water and  $\frac{1}{10}$  albumen). There are about 940 of these tubes, each divided into 2000 cells, and the organ is traversed throughout by numerous ramifications of nerves proceeding from the eighth pair. The direction of the tubes is in accordance with the opposite polarities of the two flat surfaces of the fish.

Fig. 466.

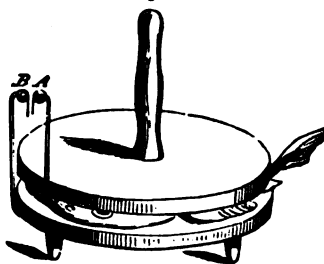


Fig. 467.



Fig. 468.

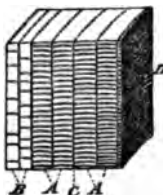


Fig. 469.



In the gymnotus, the electric organ (*fig. 468*) is of similar construction; but the tubes are rectangular and directed parallel to the axis of the fish. The transverse diaphragms, *A, B*, which are perpendicular to the length of the animal, consists of two solid membranes superposed but not in contact, one having a cellular structure, the other composed of minute fibres. There are also two liquids—one the *sub-cellular liquid*, contained between the two membranes just mentioned, the other, the *super-cellular liquid*, between two successive diaphragms. Pacini, to whom the anatomical examination of the organ is due, compares it with the voltaic battery of one metal and two liquids, the chemical action taking place between the cellular substance and the sub-cellular liquid, the super-cellular liquid acting merely as a conductor, and the fibrous substance



as the porous cell. The fibrous substance in each cell is situated towards the head of the animal, so that this mode of action is in accordance with the direction of the positive current in the body of the fish from the tail to the head.

The electrical organ of the silurus is composed of small membranes *BB* (fig. 469) crossing one another in various directions, and forming a number of octahedral cells, each having the capacity of about a cubic millimetre, and filled with an albuminous liquid. The whole forms a spongy mass just beneath the skin, and envelopes the whole body like a sac, excepting the muzzle and the fins. It is separated from the body of the fish *EE* by a thick layer of fat *DD*, which, being a non-conductor, appears to be designed to protect the animal from the effects of its own electricity.

In all the electric fishes, the action of the electric organ is to a considerable extent under the control of the will, and its exertion is attended with exhaustion of nervous energy, the animal, after giving repeated shocks, requiring rest and good nourishment to restore its electric power. But the recent experiments of Matteucci (Proc. Roy. Soc. x. 576) on the torpedo, have shown that the electric organ is not entirely under the control of the will, but is always charged, and that, round the body of the torpedo, and of every other electric fish, there is a continual circulation of electricity in the liquid medium in which the animal is immersed. In fact, when the electric organ, or even a fragment of it, is removed from the living fish and placed between the ends of a galvanometer, the needle remains deflected at a constant angle for 20 or 30 hours, or even longer.

The electric organ, or a portion of it detached from the fish and kept at the freezing temperature, preserves its electromotive power for six, or even eight days; and an organ which has been kept for 24 hours in a vessel surrounded with a mixture of ice and salt, is found to possess an electromotive power as great as that of the organ recently detached from the living fish. Thus the electric organ retains its functional activity long after nervous and muscular excitability have been extinguished. Matteucci has also shown that the electric organ may be excited by mechanical irritation, independently of nervous influence; that influence, however, renews and renders persistent the activity of the apparatus. The discharge, which is only a state of temporary activity of the organ, is brought on by an act of the will of the living animal, or by the excitation of the nerves of the organ.

#### DEVELOPMENT OF ELECTRICITY IN PLANTS.

The electric relations of the different parts of a living plant have been examined by Pouillet, Riess, Becquerel, and Wartmann, without any very definite results. The most complete experiments on the subject are those of Buff (Ann. Ch. Phys. [3] xli. 198), who has shown, that *the roots and all the internal parts of plants, which are filled with vegetable juices, are negative with regard to the more or less humid surface of the leaves, flowers, fruit, and young branches.*

The origin of this phenomenon is easily traced. The interior of the plant contains juices of various nature, which cannot pass through the epidermis, whereas that membrane is always impregnated to a certain extent with the moisture of the air. There are then in contact, a membrane impregnated with water, and vegetable organs containing liquids of various nature; if, then, a closed circuit be formed between the two, a current must necessarily be produced; this current has, however, only a very distant and indirect relation with the phenomena of vegetation.

So far, indeed, as observations have yet gone, it does not appear that living plants exhibit an electric state analogous to that which has been shown to exist in the nerves and muscles of animals, all the signs of electricity observed in them being attributable to ordinary chemical reactions, and in some cases perhaps to the electricity of the atmosphere. (De la Rive, *Traité*, iii. 82—88.)

**ELECTRICITY, ATMOSPHERIC.** The atmosphere exhibits signs of electricity in its normal state as well as during storms. A gold-leaf electroscope connected with an insulated pointed metal rod projecting into the air, gives almost constant indications of electric charge, the kind and degree of which vary with the state of the atmosphere, and the height above the surface of the earth at which the electricity is collected.

When the sky is quite cloudless and the air dry, the electricity of the atmosphere is always positive, the intensity increasing regularly with the altitude above the surface, where it is nothing. At any given altitude, the intensity of the positive charge exhibits variations, both monthly and diurnal. The monthly variations are such that the maxima of electric charge show themselves in the months when the days are shortest, and the minima in those when they are longest. The diurnal variations differ considerably in amount in different places, and are, for the most part, proportional to the variations of humidity in the air.

The precipitation of aqueous vapour in the form of cloud, fog, or rain gives rise to great and sudden changes in the electrical state of the atmosphere, the positive charge no longer following the regular course of variation above mentioned, but sometimes falling to nothing, and sometimes giving place to a negative charge of greater or less intensity. Indeed, the formation of a cloud or fog is always accompanied by a change of distribution in the electricity of the stratum of air in which it takes place. When a number of particles of aqueous vapour combine together into a vesicle or a liquid globule (see *CLOUD*, i. 1028) the small quantities of  $+E$  associated with them unite in the globule, and are accumulated on its surface, and when a number of these globules are aggregated in the form of a cloud, a considerable portion of the charge is transferred to the exterior surface. The cloud consequently acts like a charged conductor on the air below it, rendering the contiguous portion negative, and increasing the positive charge at a certain distance on either side of this negative portion. Suppose now a cloud thus charged to pass over the electroscope. When it is within a certain distance, the positive divergence of the leaves increases, then it diminishes, and at a certain time, viz. when the neutral limit between the positive and negative columns of air is passing over the electroscope, the leaves collapse; then, as the cloud passes on, they diverge with negative electricity, then again collapse, and when the cloud has passed, they again diverge with  $+E$ , showing that the air has returned to its normal electric condition. Independently, however, of this inductive action, portions of the air frequently acquire a direct negative charge, from a cause to be explained hereafter; the same cause also gives rise to the formation of negative clouds. It is easy to understand how the effects above described may be complicated by the presence of positive clouds in different parts of the sky, or of a positive cloud in one part and a negative cloud in another.

A large cloud strongly charged with  $+E$ , disturbs the electricity on the earth's surface below it, rendering the part immediately below it strongly negative, and when the opposite electricities on the ground and the lower surface of the cloud have reached a certain tension, discharge takes place between them in the form of lightning. One cloud may also act in this manner on a neighbouring cloud; and in that case, the lightning passes from one to the other without striking the earth. The discharge between two clouds may, however, affect objects on the earth's surface in this way: A positive cloud may render negative the surface of the ground below it, as well as that of a neighbouring cloud, and if discharge takes place between the two clouds, the cause which had separated the electricities of a certain portion of the earth's surface is suddenly removed, so that they recombine with equal suddenness. This is called the *return stroke*. It is not attended with any visible discharge, and is never so violent as the direct stroke of lightning, but men and animals are sometimes killed by it.

An electrified cloud never discharges all its electricity at once. This arises from the imperfect conducting power of its mass; in fact, when a number of globules of water unite to form a cloud, although a certain portion of their free electricity is transferred to the outer surface, this is not the case with the whole—because the globules are not in sufficiently close contact to form a continuous conducting mass. The charge appears rather to be distributed through the cloud in successive strata; accordingly, when an electroscope is placed in the midst of a fog or cloud driven onwards by the wind, the divergence of the leaves continually varies as strata of different intensity pass over it. An electroscope exposed to the influence of the electrified clouds during a thunderstorm, shows that every stroke of lightning, whether taking place between two clouds, or between a cloud and the earth, is preceded by a multitude of small discharges in the interior of the clouds themselves. The leaves diverge suddenly and by fits during an interval when all appears quiet; then a clap of thunder is heard; the leaves immediately collapse, and remain quiet for a time, but soon recommence their divergence, until another discharge takes place between the clouds, and so on.

Lightning assumes three different forms: the *zig-zag* or *forked lightning*, the *flash* or *sheet lightning*, and the *globe*. The first is like an ordinary electric spark, its zig-zag form being due to the cause mentioned at page 388—viz. that it seeks out the path of least resistance, striking from one collection of watery particles in the air to another; sometimes in the midst of its course it divides into two or even into three branches. Wheatstone has shown that the duration of a stroke of forked lightning, like that of the common electric spark, is less than the millionth part of a second.

Sheet-lightning is much more common than forked lightning. It has neither the whiteness nor the intense brilliancy of the latter, but is generally of a blue or violet colour, sometimes deep red; sometimes it seems to illuminate only the edges of a cloud, at other times it embraces the entire surface of the clouds, and seems to issue from the midst of them, lighting up the whole atmosphere. It probably arises from a multitude of minute discharges taking place simultaneously between the particles of a cloud, or between two clouds in the manner already mentioned.

The third kind, or globe-lightning, differs from the other two in duration, as well as



in power, being sometimes visible for one, two, or even ten seconds, passing from the clouds to the earth at a rate which the eye can easily follow. Its form is nearly spherical; in fact, it constitutes a true ball of fire, which sometimes splits up into several pieces as it falls, rebounding several times from the earth, sometimes exploding with a report like the discharge of several pieces of ordnance, and scattering streams of forked lightning in all directions. It is less common than the two former kinds, but appears to be the form which lightning generally assumes when it penetrates into the interior of a building.

It is clear that this form of lightning is of very different nature from forked and sheet lightning; in fact, it cannot be a mere electric spark, but probably consists of a portion of moist air or vapour condensed and strongly electrified: in fact, a small cloud charged so intensely as to become luminous. De la Rive suggests that it may contain a mixture of air and hydrogen gas, resulting from the decomposition of aqueous vapour by previous electric discharges, and that when it comes into the line of a stroke of lightning, or when its own electric charge becomes high enough to produce a spark, it explodes. The explanation is not very probable: for the electric discharges in the air, even if they did resolve the aqueous vapour into oxygen and hydrogen, would cause the gases instantly to recombine.

Thunder is the noise resulting from the violent concussion of the air attending the electric discharge. The reverberation or roll arises from the manner in which the discharge takes place, which, as already observed, is not instantaneous, but consists of a great number of comparatively small discharges, sometimes accompanied by a great one; but even an instantaneous lightning-stroke will not generally produce a mere instantaneous report, because the different parts of the line, even when it is vertical, and still more when it is horizontal, are situated at different distances from the observer. The reflection of the sound-waves from the clouds doubtless also adds to the effect; among mountains, the reverberation is very much increased by the echoes thus produced.

*Source of Atmospheric Electricity.*—Volta and Saussure attributed the electricity of the atmosphere to the evaporation of water from the surface of the earth. Pouillet took a similar view, excepting that he regarded the electric charge as arising, not from the mere evaporation of the water, but from the decomposition of a saline solution—viz. sea-water, the water escaping in vapour and the salt remaining behind. We have seen, however (p. 429), that it is only when the evaporation is very rapid, that any signs of electricity can be thus obtained, as, when it takes place slowly, the separated electricities have time to recombine before the water escapes.

It seems necessary, therefore, to look to some more general cause for the development of atmospheric electricity. The action of the sun upon the atmosphere, and the consequent unequal distribution of temperature therein, has been suggested as a cause; but we have no proof that gases and vapours exhibit the slightest trace of thermo-electricity.

De la Rive ascribes the electric charge of the atmosphere to chemical action taking place on the inner surface of the solid crust of the earth, where it is in contact with the internal incandescent mass, this action proceeding partly from local causes, but chiefly from the infiltration of sea-water, in consequence of which the water acquires a positive, the solid part of the earth a negative charge (p. 414). The whole mass of sea-water thus becoming positive, the vapours which rise from it are also positive, and communicate a positive charge to the atmosphere. This evaporation takes place over the whole surface of the ocean, but most abundantly in the tropical regions; and the positively-charged vapours rising at first in these regions more or less vertically, are afterwards carried away towards the poles by the tropical current (the return trade-wind) in the higher regions of the atmosphere. This current, travelling at first horizontally, bends down more and more to the earth as it approaches the poles, and becomes cooler; and in the polar regions themselves it comes nearly down to the negatively-charged surface of the earth, whence results a discharge of electricity, constituting the *aurora borealis* or *australis*.

The greater amount of evaporation taking place in the hemisphere in which the sun is situated, accounts for the greater prevalence of storms during summer; in winter, on the other hand, the positively-charged vapours descend nearer to the ground; hence the greater intensity of the permanent charge of the atmosphere during the winter months.

The solid crust of the earth being negative, the vapours rising from it and from ponds and rivers on its surface must also be negative. This is another cause of the diminution of the permanent positive charge of the atmosphere in summer, and likewise accounts for the formation of negative clouds. As these negative clouds play a considerable part in the production of thunderstorms, the occurrence of a greater number of storms during the summer season in temperate climates is easily accounted for; in the



tropical regions, where evaporation from the surface of the ground is more abundant, and goes on at much the same rate all the year through, storms are of constant occurrence. Over large expanses of water, such as the great oceans, at a long distance from land, thunderstorms rarely occur, because no negatively-charged vapours are poured into the atmosphere.

That the water of the ocean and the solid crust of the earth are actually in opposite electrical states has been proved by the observations of Peltier (*Ann. Ch. Phys.* [3] iv. 385), and of Becquerel (*Compt. rend.* xlii. 661); this opposition of electric states likewise accounts for the fact that the air is positive in immediate contact with the surface of the sea, whereas over planes far from the sea, the positive charge shows itself above a certain height only.

The development of electricity by the chemical action of sea-water on the fused matter below the solid crust of the earth appears also to be the origin of the intense signs of electric action which usually accompany volcanic eruptions. In the eruption of Vesuvius in 1794, clouds were emitted which gave out flashes of lightning, accompanied by loud peals of thunder, and many houses were struck by the lightning. The observations of Palmieri (*Arch. des Sc. Phys.* xxxvi. 105) have shown that the vapours emitted from the crater of Vesuvius are charged with positive electricity.

**ELECTRODES.** The terminals, metallic or otherwise, which convey an electric current into a liquid (p. 432).

**ELECTRO-DYNAMICS.** The science which treats of the mutual action of electric currents, and of electric currents and magnets (pp. 442, 446).

**ELECTROLYSIS.** Decomposition by electricity (pp. 397, 432).

**ELECTROLYTE.** A compound liquid decomposable by electricity (pp. 397, 432).

**ELECTRO-MAGNETISM.** The branch of electro-dynamics which treats of the mutual action of the magnet and the electric current.

**ELECTROMETER.** An instrument for measuring the strength or degree of the electric charge of a body (p. 330).

**ELECTRO-MOTIVE FORCE.** This term, originally employed by Volta to signify the force which, as he supposed, gave rise to the separation of the two electricities at the point of contact of two dissimilar metals, is now applied to any source of electric excitement whatever, but is used for the most part in speaking of arrangements which generate a continuous current of electricity.

**ELECTROMOTOR.** Any arrangement by which a current of electricity is generated.

**ELECTRO-NEGATIVE** and **ELECTRO-POSITIVE.** Terms used to denote the relative position of bodies in the electric series (p. 432).

**ELECTRO-NITROGENETS.** *Alloys of Ammonium.* Many metallic salts—as those of gold, silver, cadmium, &c.—when electrolysed in presence of ammoniacal salts, yield at the negative electrode, metallic deposits containing nitrogen, which have not been accurately investigated, but are supposed by Grove (*Phil. Mag.* [4] xix. 19) to be ammonium-compounds.

**ELECTROPHORUS.** See page 385.

**ELECTRO-PLATING.** The coating of metals with silver by electrolysis. (See *Ure's Dictionary of Arts, Manufactures, and Mines*, art. **ELECTRO-METALLURGY**, ii. 95.)

**ELECTROSCOPE.** An instrument for detecting the existence of an electric charge, and indicating its nature, whether positive or negative (pp. 380, 424).

**ELECTROTYPE.** The deposition of metals in the compact state by electrolysis, so as to form casts or models. (See *Ure's Dictionary of Arts, Manufactures, and Mines*, art. **ELECTRO-METALLURGY**.)

**ELECTRUM.** A term applied to those native alloys of gold and silver, which contain sufficient silver to make their colour perceptibly lighter and their specific gravity considerably less than that of pure gold. Hausmann (*Handb. d. Miner.* ii. 25) applied it to such as contain from 20 to 50 per cent. silver. According to C. Rammelsberg, alloys containing not more than 20 per cent. silver are completely decomposed by nitro-muriatic acid, whereas those which are richer in silver, do not readily yield up their gold to that reagent. Before the blowpipe, gold containing silver yields an opalescent glass with phosphorus-salt; a larger proportion of silver renders the glass yellow and opaque.

**ELEMENTARY ANALYSIS.** See ANALYSIS, ORGANIC (i. 225).

**ELEMENTS.** *Elementary Bodies. Simple Substances. Grundstoffe, Urstoffe.* By these terms we understand substances which cannot be, or rather which have not hitherto been, resolved into more simple forms of matter. To the list of elementary bodies given in the article ATOMIC WEIGHTS (i. 465), we must now add three, discovered since that article was written, viz. Cæsium and Rubidium, discovered by Bunsen, and Thallium, by Crookes. The number of elements at present known with certainty is 62; two others, Dianium (p. 318) and Norium, may be mentioned as of uncertain existence. The list will doubtless be increased by future researches, especially by the new method of spectrum analysis, which has already led to the discovery of the three elements above mentioned, cæsium, rubidium, and thallium. But it is scarcely probable that any element existing in considerable quantity in the earth's crust yet remains to be discovered. The elements which constitute the great mass of the earth's crust are, indeed, comparatively few, viz. *aluminium, calcium, carbon, chlorine, hydrogen, magnesium, oxygen, potassium, silicium, sodium, sulphur.* The last of these has been known from the remotest times, and the rest were discovered in the early days of modern chemistry. The more abundant metals, iron, copper, lead, which occur chiefly in veins in the older rocks, have likewise been known from remote antiquity. Most of the other elements, the discovery of which is of comparatively recent date, occur but sparingly, and many of them only in extremely small quantity, *e. g. thorium, tantalum, tellurium, ruthenium, cæsium, and rubidium.*

The elements are usually divided into two classes, Metals and Metalloids, which, however, like most divisions of natural objects, blend into each other by insensible degrees. The metals for the most part form basic oxides; the metalloids, acid or indifferent oxides. The compounds of metals with each other possess the metallic lustre; those of metalloids with one another, or with the metals, do not for the most part exhibit that lustre.

The elements may be divided into groups or families resembling one another more or less in their chemical characters and crystalline forms (see ISOMORPHISM). The members of the same group generally occur together in nature; and minerals containing one of them, as principal constituent, usually contain also small quantities of the other elements of the same group. Examples of these groups are:—

Oxygen	Chlorine	Nitrogen	Chromium	Silicium	Barium
Sulphur	Bromine	Phosphorus	Vanadium	Titanium	Strontium
Selenium	Iodine	Arsenic	Molybdenum	Tantalum	Calcium
Tellurium	Fluorine	Antimony	Tungsten	Niobium	Magnesium
Cerium	Iron	Cadmium	Potassium	Platinum	
Lanthanum	Cobalt	Zinc	Sodium	Palladium	
Didymium	Nickel		Lithium	Rhodium	
	Manganese		Cæsium	Iridium	
			Rubidium	Ruthenium	
				Osmium	

Many of the elements which resemble one another closely in their chemical relations, have also nearly equal atomic weights, *e. g.* iron, manganese, cobalt and nickel; cerium and lanthanum; platinum and iridium; rhodium and ruthenium. On the other hand, instances of this equality of atomic weights exist between elements which exhibit no such resemblance of properties, *e. g.* molybdenum and cerium; osmium and mercury; tantalum, vanadium, and barium.

The members of some of the preceding groups exhibit nearly equal differences in their atomic weights. Thus a difference of 24 is exhibited by the atomic weights of calcium 20, strontium 44, and barium 68; a difference of 48 by sulphur 32, selenium 80, and tellurium 128; of 16, by lithium 7, sodium 23, and potassium 39. The atomic weights of other groups exhibit nearly equal differences, *e. g.* chlorine 35.5, bromine 80.4, and iodine 127.0; also phosphorus 31, arsenic 75, and antimony 120.

Other relations between the atomic weights of elements have been pointed out by Kramers (Pogg. Ann. lxxxv. 56); Low (Sill. Am. J. [2] xvii. 387); Lessen (Ann. Ch. Pharm. ciii. 121); Gladstone (Phil. Mag. [4] v. 313); and Dumas (Ann. Ch. Pharm. cv. 74; cviii. 324).

**ELEM.** A resin of which several kinds occur in commerce. Ordinary or West Indian elemi, *Elemi occidentale*, is said to be the produce of *Icica icicaria*, Dec. (*Amars clemifera*, L.); East Indian elemi, *Elemi orientale*, which is more esteemed, but rarely met with, is said to be obtained from *Amars ceylonica* or *Balsamodendron ceylonicum*, Kunth. According to Landerer, an African elemi, *Elemi aegyptiacum*, s. *athiopium*, is sometimes sold at Smyrna and Constantinople: it is said to be imported from Nubia and Egypt, and is perhaps the produce of *Elæagnus hortensis*.

Common elemi forms more or less translucent masses, having a fatty lustre and yellowish or brownish-yellow colour; it is soft when fresh, but gradually hardens. It shines in the dark when rubbed or warmed. It is chiefly used as an ingredient of varnishes, especially of spirit and turpentine varnishes, which it prevents from cracking as they dry.

Elemi resin is a mixture of an amorphous acid resin easily soluble in cold alcohol and a crystallisable indifferent resin, soluble in cold, and sparingly soluble in boiling alcohol, together with variable quantities of a volatile oil, and foreign matters, including ash (2 or 3 per cent.)

The resin soluble in cold alcohol contains, according to Johnston (Ann. Ch. Pharm. xlv. 338), 78.7 per cent. carbon and 10.5 hydrogen, agreeing nearly with the formula  $C^{20}H^{22}O^4$ , or  $C^{20}H^{22}O^2$ ; this substance forms about  $\frac{2}{3}$  of the entire resin.

When the remaining portion of the resin is boiled with alcohol, and the solution left to evaporate, a considerable quantity of a crystalline resin is deposited, which may be purified by repeated crystallisation from alcohol. It forms a white confusedly crystallised mass, perfectly soluble in strong boiling alcohol, and forming a solution neutral to litmus paper.

According to analyses by H. Rose (Ann. Ch. Pharm. xxxii. 93; xl. 307), and Johnston (*loc. cit.*), this crystalline resin appears to have the composition  $C^{20}H^{22}O$ ; those of Hess (Ann. Ch. Pharm. xxix. 139) agree rather with the formula  $C^{20}H^{22}O^2$  or  $C^{20}H^{22}O$ , which is more probable.

			Hess.		Ross.		Johnston.
C <sup>20</sup>	.	240 .	83.3 .	83.8 .	81.7	84.5 .	85.2
H <sup>22</sup>	.	32 .	11.1 .	11.5 .	11.2	12.8 .	11.9
O	.	16 .	5.6 .	4.7 .	7.1	2.7 .	2.9
		<u>288</u>	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>

The analyses agree nearly with that of the constituent of animé resin, examined by Laurent, and with that of arbol-a-brea resin, analysed by Dumas. (Baup's *amyrin*, i. 364.)

The alcoholic solution of elemi resin is not clouded by alcoholic potash, but is precipitated by aqueous potash. Ammonia added to the alcoholic solution converts it into a gelatinous mass. The alcoholic solution is not precipitated by alcoholic acetate of lead or nitrate of silver, even the addition of a drop of ammonia causing no precipitate, but only a slight turbidity.

Crystallised elemi resin is decomposed and charred by dry distillation, yielding first a viscid, brown, acid oil, having an agreeable odour, afterwards a black, disagreeably smelling tar.

**Oil of Elemi.—Elemine.** Elemi resin distilled with water yields a transparent colourless oil, having the composition of a camphene,  $C^{10}H^{16}$ . It has an agreeable odour like that of the resin, and a faint taste. Specific gravity = 0.852 at 24° C. (Stenhouse), 0.849 at 11° C. (Deville). Boiling point 166° C. (Stenhouse), 174° C. (Deville). Vapour-density = 4.0. Index of refraction = 1.47 at 14° C. (Deville). Optical rotatory power, 90° 30'.

Oil of elemi is insoluble in water, but easily soluble in alcohol and ether. With hydrochloric acid, it forms two isomeric compounds,  $C^{10}H^{16}.HCl$ , one solid, the other liquid; the solid compound is optically inactive. With iodine, nitric acid, and sulphuric acid, oil of elemi behaves like oil of turpentine; it is also similarly affected by heat. The proportion of volatile oil in the resin probably varies according to its age. Bonastre found 12.5 per cent., Stenhouse only 3.5 per cent. oil; good elemi resin contains, according to Deville, more than 13 per cent. oil. (Stenhouse, Ann. Ch. Pharm. xxxv. 304; Deville, *ibid.* lxxi. 352.)

**ELEMINE.** Syn. with OIL of ELEMINE.

**ELEPHANT'S FAT**, according to Filhol and Joly (Compt. rend. xxxv. 393), is white, soft, inodorous, melts at 28° C., contains 79 pts. liquid, and 21 pts. solid fat (stearin and palmitin): the liquid fat is easily soluble in alcohol, does not dry up on exposure to the air, and is not solidified by hyponitric acid.

**ELEPHANT'S URINE**, according to Brandes (Arch. Pharm. xviii. 64), contains hippuric acid and urea, together with alkaline and earthy phosphates and carbonates. Purree or Indian yellow is said to be formed from elephant's urine.

**ELUYARITE.** A name sometimes applied to the allophane of Friesdorf, near Bonn.

**ELIQUATION.** An operation by which a more fusible substance is separated from another which is less fusible, namely, by the application of a degree of heat sufficient to melt the former, but not the latter. (See COPPER, p. 32.)



**ELIASITE.** A mineral consisting of hydrated uranic oxide, mixed with several foreign substances, but forming, according to W. Haidinger, a distinct species. It occurs in the Elias mine, near Joachimsthal, in Bohemia, in flattened pieces of a dark reddish-brown colour, translucent on the edges, and with a waxy lustre. It is brittle, has a specific gravity = 4.129, and hardness = 3.5. According to Ragsky's analysis (*Kenngott's Uebersicht*, 1852, p. 81), it contains 61.38 per cent.  $UO_3$ , 10.68  $H_2O$ , 1.17  $Al_2O_3$ , 6.63  $FeO$ , 1.09  $Fe_2O_3$ , 3.09  $CaO$ , 2.20  $MgO$ , 4.62  $PbO$ , 5.13  $SiO_2$ , 2.52  $CO_2$ , 0.84  $P_2O_5$ , and a trace of arsenic. The carbonic acid is perhaps combined with the lime and magnesia, making up 5.7 per cent.

**ELLAGIC ACID.** *Bezoardic acid.*— $C^{14}H^4O^6 = \left\{ \begin{smallmatrix} C^{14}H^4O^6 \\ H^2 \end{smallmatrix} \right\} O_2$ . In the crystallised state,  $C^{14}H^4O^6 \cdot 2H_2O$ . (Chevreul [1815], *Ann. Ch. Phys.* [2] ix. 629. Braconnot, *ibid.* 187. Pelouze, *ibid.* liv. 367. Taylor, *Phil. Mag.* [3] xxiv. 354. Lipowitz, *Simon's Beiträge zur. physiol. u. pathol. Chemie.* i. 464. Wöhler and Merklein, *Ann. Ch. Pharm.* lv. 129.)

Ellagic acid exists as a constituent of certain animal concretions; it is also a product of the decomposition of gallic acid. According to Chevreul, when a solution of gall-nuts is exposed to the air, a grey powder is deposited. This is exhausted by boiling water, which extracts gallic acid; the residue is treated with potash, and the ellagic acid thereby dissolved, is precipitated by a mineral acid.

The acid is contained in largest quantities in certain animal concretions called oriental bezoars. They are found of different sizes, from that of a bean to that of an egg.

To obtain the acid, the bezoars are dissolved in strong caustic potash, care being taken not to heat the mixture, and to prevent access of air as much as possible. As soon as the whole is dissolved, a current of carbonic acid is passed through the clear liquid. In this way, ellagate of potassium is precipitated as a whitish powder. It is filtered, washed, and pressed, recrystallised from boiling water, and the acid is separated by throwing the solution into concentrated hydrochloric acid.

Pure ellagic acid is a light, pale yellow, tasteless powder, seen under the microscope to consist of transparent prisms. At an elevated temperature, it decomposes without melting, and the carbonised mass is covered with crystals. It is insoluble in water, but dissolves in alcohol to a pale yellow liquid, having a slight acid reaction. It gives off 2 at. of water, at  $100^\circ C$ .

*Sulphuric acid* dissolves ellagic acid without alteration; water precipitates it unchanged. *Nitric acid* converts it into oxalic acid. *Iodic acid* converts it into a peculiar acid, with rapid evolution of carbonic acid, and separation of iodine. A neutral aqueous solution of *ferrie chloride* is coloured by ellagic acid, greenish at first, but ultimately becomes bluish-black and opaque, like ink, the solution then containing ferroso-ferrie salts.

The ellagates are little known; many of them appear to be basic salts.

*Potassium-salt.*  $C^{14}H^4K^2O^6$ . A light powder, consisting of microscopic prisms. Another salt is obtained as grey powder, consisting of microscopic crystals, by digesting ellagate of potassium in alcoholic potash. It appears to be a basic salt  $C^{14}H^4K^2O^6$ .  $KHO$ .

A solution of ellagic acid in moderately strong potash exposed to the air, gradually changes colour, and deposits dull-black crystals. Wöhler and Merklein call this body *glaucomelinate of potassium*. When it is boiled with water, ellagate of potassium is reproduced. The composition of the salt is represented to be  $C^{12}H^4K^2O^6$ , which appears improbable, from the fact of the regeneration of ellagic acid by water. Besides glaucomelinate, the solution contains carbonate, oxalate, and another soluble potassium-salt.

*Ellagate of Sodium*,  $C^{14}H^4Na^2O^6$ , is a pale yellow crystalline powder, less soluble than the potassium salt.

*Barium-salt.*  $C^{14}H^4Ba^2O^6 \cdot BaHO$ . Insoluble lemon-yellow compound.

*Lead-salt.*  $C^{14}H^4Pb^2O^6 + PbO$ . Amorphous yellow precipitate, which by drying becomes olive green. E. A.

**ELUTRIATION.** The separation of the lighter from the heavier particles of a pulverulent mixture by washing.

**EMBOLITE.** A chloro-bromide of silver,  $Ag^2Br^2Cl^2$ , found abundantly in Chile, also at Eulalia in Chihuahua, Mexico, and at Colula, Honduras. It occurs crystallised in cubes and cubo-octahedrons; also massive. Specific gravity 5.31–5.43 (Domeyko), 5.53 (Yorke), 5.81 (Breithaupt). Hardness = 1–1.5. It is perfectly malleable; has a resinous and somewhat adamantine lustre, and varies in colour from asparagus-green to pistachio, olive, and greyish-green. Plattner (*Pogg. Ann.* lxxvii. 134) found in it 66.86 per cent. silver, 20.09 bromine, and 13.05 chlorine, the

formula requiring 67.0 Ag, 19.8 Br, and 13.2 Cl. Domeyko (*Elementos de Mineralogia*, 1845, p. 203) found 51.0 and 52.8 per cent. AgCl; 49.0 and 47.2 AgBr. Yorke (Chem. Soc. Qu. J. iv. 2) found 53.2 AgCl and 46.8 AgBr.

**EMBRITHITE.** Breithaupt's name for a sulphantimonite of lead from Nertschinsk, of specific gravity 6.3, containing 53.3 per cent. lead, 0.8 copper, 0.04 silver; probably identical with Boulangerite.

**EMERALD.** The bright green transparent variety of beryl (i. 581), much prized as a gem. The colour is usually attributed to oxide of chromium, of which Vauquelin found 3.50, and Klaproth 6.30 per cent. in emeralds from Santa Fe de Bogota. Lewy, however (Ann. Ch. Phys. [3] liii. 3), found that an emerald from the same locality contained only a trace of chromic oxide, and was rendered quite colourless by ignition. Hence he attributes the green colour to organic matter, which, according to his analysis, exists in the mineral to the amount of 0.12 per cent., going off at a red heat, together with 1.66 per cent. water. According to Hofmeister, on the other hand (J. pr. Chem. lxxvi. 1), emeralds (from the Pinzgau) retain their colour after ignition. The analyses of the (ignited) emerald by Lewy and Hofmeister are as follows:—

SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Gl <sup>2</sup> O	Cr <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	Ca <sup>2</sup> O	Mg <sup>2</sup> O	Na <sup>2</sup> O	
67.85	17.95	12.40	trace	.	.	0.90	0.70	= 99.80. Lewy.
66.22	16.36	12.79	.	1.63	0.78	0.83	.	= 98.61. Hofmeister.

**EMERALD NICKEL.** A native hydrocarbonate of nickel. (See CARBONATES, i. 789.)

**EMERALDINE**, or *Aniline-green*. See DYING (p. 358).

**EMERY.** The opaque crystallo-granular variety of corundum (p. 86), used for grinding, cutting, and polishing glass, metals, enamels, and other hard substances. (See *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 121.)

**EMERYLITE.** Syn. with MARGARITE.

**EMETINE.** An alkaloid which forms the active principle of ipecacuanha root. It was discovered in 1807 by Pelletier and Magendie (Ann. Ch. Phys. [2] iv. 172) and further examined by Buchner (Repert. Pharm. vii. 289), and by Dumas and Pelletier (Ann. Ch. Phys. [2] xxiv. 180), who give the following process for obtaining it:—

The powder of ipecacuanha is digested in water with calcined magnesia; the deposit is thrown on a filter, washed carefully with very cold water, and dried; and the emetine is then taken up by alcohol. It may be afterwards combined with an acid, and the salt may be purified with animal charcoal. When the emetine is once more thrown down by magnesia, alcohol redissolves it in a colourless state.

Emetine thus obtained is yellowish-white, pulverulent, and is but slightly coloured by exposure to the air. It is little soluble in cold water, and somewhat more so in hot water. It melts about 50° C. It is very soluble in alcohol, but not in ether or in oils. Its constituents are, carbon 64.57 p.c., nitrogen 4.30, hydrogen 7.77, oxygen 23.36 (Dumas and Pelletier). Emetine is highly alkaline, though acids saturated with it do not afford crystallisable compounds. Gallic acid and nut-galls form with it very abundant white precipitates. Basic acetate of lead has no effect on it.

Strong nitric acid transforms emetine into a yellow resinous substance, and oxalic acid.

Emetine taken internally excites vomiting, 3 milligrammes being sufficient to produce this effect.

The *oxalate* and *tartrate* of emetine are very soluble in water. The *chloromercurate* and *chloroplatinate* are very sparingly soluble. The *gallotannate* is a white flocculent precipitate, soluble in alkalis; it is neither emetic nor poisonous.

**EMONITE.** Syn. of STRONTIANITE, or native CARBONATE OF STRONTIUM (i. 797).

**EMODIN.** C<sup>15</sup>H<sup>10</sup>O<sup>12</sup>.—A constituent of rhubarb root, discovered by Warren De la Rue and Hugo Müller (Chem. Soc. Qu. J. x. 304). When crude chrysophanic acid, obtained as described at p. 959, vol. i., by treating the root with benzene, is redissolved in hot benzene, emodin remains behind, in the form of a reddish-yellow substance, an additional quantity separating from the solution as it cools. It may be purified by crystallisation from hot glacial acetic acid, and afterwards from boiling alcohol.

Emodin thus prepared crystallises in long, brittle, concentrically-grouped monoclinic prisms of a deep orange-red colour. It melts above 250° C., a small portion volatilising at the same time undecomposed. Chemically it resembles chrysophanic acid, but is much more soluble in alcohol, glacial acetic acid, and amyl alcohol, less soluble in benzene. With caustic alkalis, it behaves like chrysophanic acid.



Emodin gives by combustion 66.63 per cent. carbon and 4.10 hydrogen, agreeing nearly with the empirical formula  $C^{10}H^{13}O^{13}$ , or  $C^{10}H^{20}O^{13}$  (66.85 C. and 4.18 H.).

**EMPLECTITE.**  $Cu^2BiS^2$  or  $CuBiS^2$ .—A mineral from Tannenbaum in the Erzgebirg, containing 18.83 per cent. sulphur, 62.6 bismuth, and 18.72 copper; forming needle-shaped rhombic crystals of light grey to tin-white colour and metallic lustre. (Schneider, Pogg. Ann. xc. 166.—Dauber, *ibid.* xcii. 241.—Kenngott, *Uebersicht*. 1853, p. 125.)

**EMPYREUMA.** The peculiar smell produced by distilling vegetable or animal substances in closed vessels, or by burning such substances with imperfect access of air.

**EMULSIC ACID.** An acid said to be formed by boiling emulsin with alkalis, ammonia being given off at the same time. (Thomson and Richardson.)

**EMULSIN.** *Synaptase*. (Robiquet, J. Pharm. xxiv. 326.—Thomson and Richardson, Ann. Ch. Pharm. xxix. 180.—Ortloff, Arch. Pharm. xlviii. 16.—Bull, Ann. Ch. Pharm. lxi. 145.)—A neutral substance contained in sweet and in bitter almonds, and possessing the power of acting as a ferment on the amygdalin of the latter in presence of water, converting it into hydride of benzoyl, hydrocyanic acid, and glucose (i. 292).

To obtain emulsin, sweet almond paste, well freed from fixed oil, is macerated in three times its weight of pure water, the mass is pressed, and the emulsion thus obtained is left to itself at 20° or 25° C. After the lapse of a day, the emulsion is found to have separated into two layers, the upper of which is coagulated, and looks like cream, while the lower is watery and transparent. After two or three days, this watery liquid no longer gives a precipitate of casein with acetic acid, but it forms with alcohol a precipitate perfectly soluble in water. This last precipitate consists of emulsin; after being washed with absolute alcohol and dried in vacuo over sulphuric acid, it forms a white, opaque, friable mass, soluble in water. It is difficult, however, to obtain emulsin quite free from colouring matter, the process succeeding only when performed on small quantities of material.

The property of being precipitated by alcohol does not belong to emulsin itself, but is due to the phosphates which it holds in solution, and from which it cannot be separated. Emulsin possesses a decided acid reaction, and it is this acidity which enables an emulsion of almonds to hold the phosphates in solution.

An aqueous solution of emulsin when boiled deposits a white granular precipitate, which on cooling redissolves completely in the supernatant liquid. This precipitate contains a considerable quantity of inorganic matter, consisting of phosphate of magnesium with a little phosphate of calcium; the filtered liquid contains the products of decomposition of the emulsin, which, strictly speaking, does not coagulate by heat, but is completely decomposed. (Bull.)

Emulsin completely loses the power of transforming amygdalin into hydride of benzoyl, when its aqueous solution is boiled; but it retains this power when heated to 100° C. in the dry state, even for several hours.

The aqueous solution of emulsin is completely precipitated by acetate of lead; the filtrate no longer acts on amygdalin, but the lead-precipitate effects the complete transformation of this substance into hydride of benzoyl.

The solution of emulsin exposed to the air for several days at common temperatures putrefies, giving off gas and becoming turbid; nevertheless it retains for a long time the power of acting on amygdalin.

Lactic acid is found among the products of the decomposition of emulsin.

The analysis of emulsin gives the following results:—

	Thomson and Richardson.		Bull.		
	48.78	48.40	43.59	43.74	42.75
Carbon . . . . .	48.78	48.40	43.59	43.74	42.75
Hydrogen . . . . .	7.79	7.68	6.96	7.33	7.37
Nitrogen . . . . .	18.81	18.64	11.64	11.40	11.52
Sulphur . . . . .	1.25		1.25		
Oxygen . . . . .	24.62	25.28	36.56	37.53	38.36
	100.00	100.00	100.00	100.00	100.00

Thomson and Richardson do not mention the existence of sulphur or of mineral matter. Bull found quantities of ash varying from 22 to 35.8 per cent.; in the three analyses above given the ashes are deducted.

**EMULSION.** An imperfect combination of oil and water, by the intervention of some other substance capable of combining with both these liquids. Such substances are either saccharine or mucilaginous.

U.



**EMYDIN.** A substance contained in the yolk of turtle's eggs. It forms white, hard, transparent grains, very soluble in dilute potash; swells up in acetic acid without dissolving; dissolves in boiling hydrochloric acid without violet coloration. Contains 49·4 per cent. carbon, 7·4 hydrogen, and 14·6 nitrogen, together with phosphorus and oxygen. It approaches in composition to the ichthin of the eggs of certain fishes. It yields about 1 per cent. of ash. (Valenciennes and Fremy.)

**ENALLOCHROME.** Syn. with *ÆSCULIN*.

**ENAMEL.** There are two kinds of enamel, the opaque, and the transparent. Transparent enamels are usually rendered opaque by adding putty, or the white oxide of tin, to them. The basis of all enamels is a perfectly transparent and fusible glass. The oxide of tin renders this of a beautiful white, the perfection of which is greater when a small quantity of manganese is likewise added. If the oxide of tin be not sufficient to destroy the transparency of the mixture, it produces a semi-opaque glass, resembling opal.

Yellow enamel is formed by the addition of oxide of lead, or of antimony. Kunckel likewise affirms, that a beautiful yellow may be obtained from silver.

Red enamel is afforded by the oxide of gold, and also by that of iron. The former is the most beautiful, and stands the fire very well, which the latter does not.

Red oxide of copper likewise yields a very fine red colour, but it is somewhat difficult to manage, on account of its tendency to pass into the higher oxide.

Black oxide of copper affords a green; manganese, a violet; cobalt, a blue; and iron, a very fine black. A mixture of these different enamels produces great variety of intermediate colours, according to their nature and proportion. In this branch of the art, the coloured enamels are sometimes mixed with each other, and sometimes the oxides are mixed before they are added to the vitreous bases.

In the Transactions of the Society of Arts for 1817, a valuable list of receipts for enamel colours is given by Mr. R. Wynn, for the communication of which a premium was awarded. The following are Mr. Wynn's fluxes:—

	Parts.		Parts.
No. 1. Red lead . . . .	8	No. 3. Red lead . . . .	1
Calced borax . . . .	1½	Flint glass . . . .	3
Flint powder . . . .	2	No. 4. Red lead . . . .	9½
Flint glass . . . .	6	Borax not calced . . . .	5½
		Flint glass . . . .	8
No. 2. Flint glass . . . .	10	No. 5. Flint glass . . . .	6
White arsenic . . . .	1	Flux, No. 2 . . . .	4
Nitre . . . .	1	Red lead . . . .	8

After the fluxes have been melted, they should be poured on a flag-stone wetted with a sponge, or into a large pan of clean water, then dried, and finely pounded in a biscuit-ware mortar for use.

*Yellow enamel:*—Red lead 8 pts.; oxide of antimony 4 pts.; white oxide of tin 1 pt.

Mix the ingredients well in a biscuit-ware mortar, and, having put them on a piece of Dutch tile in the muffle, make it gradually red-hot, and suffer it to cool. Take of this mixture 1, of flux No. 4, 1½; grind them in water for use. By varying the proportions of red lead and antimony, different shades of colour may be obtained.

*Orange enamel:*—Red lead 12 pts.; red sulphate of iron 1 pt.; oxide of antimony 4 pts.; flint powder 3 pts.

After calcining these without melting, fuse 1 part of the compound with 2½ of flux.

*Dark red enamel:*—

	Parts.	<i>Light red enamel:</i> —	Parts.
Sulphate of iron calcined dark . . . .	1	Red sulphate of iron . . . .	1
Flux No. 4, 6 pts. } of this . . . .	3	Flux No. 1. . . .	3
Colcothar 1 pt. }		White lead . . . .	1½

*Brown enamel:*—Manganese 2½ pts.; red lead 8½ pts.; flint powder 4 pts.

See Transactions of the Society, or Phil. Mag. vol. li. Mr. Tilloch observes, that borax should be used sparingly, as it causes efflorescence and decay of the enamel colours. For further details, see *Ure's Dictionary of Arts, Manufactures, and Mines*, ii. 125. U.

**ENARGITE.** A sulpharsenate of copper originally found at Morococha, in the Cordilleras of Peru, where it is largely worked as a copper ore, and occurs in large masses, occasionally also in small drusy crystals imbedded in crystalline limestone, together with Tennantite (Breithaupt, Pogg. Ann. lxxx. 383). It is also found in Brewer's mine, Chesterfield county, South Carolina (Genth, Sill. Am. J. [2] xxiii. 420), in the

mines near Santa Anna in New Granada (W. J. Taylor, *ibid.* xxvi. 349), and in the Cordilleras of Chile (Field, Chem. Soc. Qu. J. xii. 9; Sill. Am. J. [2] xxvii. 52, 387.) The mineral from this last locality was originally regarded by Field as a distinct species, and named by him *Guayaconite*.

The mineral from Morococha exhibits the following properties:—The crystals are trimetric, with the faces  $\alpha P$ .  $\alpha P$ .  $\alpha P\infty$ .  $\alpha P\infty$ . Angle  $\alpha P$ :  $\alpha P$  =  $98^\circ 11'$ . Cleavage perfect parallel to  $\alpha P$ , distinct parallel to  $\alpha P\infty$  and  $\alpha P\infty$ , indistinct parallel to  $\alpha P$ . Specific gravity = 4.43 to 4.45 (Breithaupt); 4.362 (Kenngott). Hardness = 3. Lustre metallic. Colour iron-black. Streak black. Brittle. Fracture uneven. (Breithaupt.)

Decrepitates when heated, and in a tube yields a sublimate of sulphur and sulphide of arsenic; melts easily before the blowpipe, giving off arsenic-vapours and forming a white deposit on the charcoal; the roasted assay exhibits the reactions of copper. Soluble in nitro-muriatic acid. In the state of powder it is partly decomposed by potash-ley, and acids added to the solution throw down sulphide of arsenic containing antimony. (Plattner, Pogg. Ann. lxxx. 383.)

*Analyses.* a. From Morococha (Plattner) *loc. cit.*—b. From South Carolina (Genth).—c. From New Granada; colour and streak greyish black (Taylor).—d. From Chile: specific gravity = 4.39; hardness = 3.5 to 4 (Field).

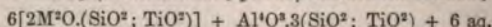
	S.	As.	Sb.	Cu.	Fe.	Zn.	Ag.
a.	32.22	17.69	1.61	47.20	0.57	0.23	0.72 = 99.45
b.	33.78	15.63	. .	50.59	. .	. .	. . = 100.00
c.	34.50	16.31	1.29	46.62	0.27	. .	. . = 98.99
d.	31.82	19.14	. .	48.50	trace	. .	trace = 99.46

These analyses agree nearly with the formula of a tricuprous sulpharsenate,  $\text{Cu}^3\text{AsS}_4$  (calc. 32.53 sulphur, 18.82 arsenic, and 48.60 copper).

**ENCELADITE.** *Warwickite*.—An ore of titanium found in the dolomite of Amity (New York), together with spinelle, titaniferous iron, and chondrodite. Externally it resembles warwickite. Oblique rhombic prisms (? monoclinic) having a blue-black or brown-black colour, with bluish streak. Lustre varying from resinous to metallic. Hardness = 3 to 4. Specific gravity 3.188. Heated in a tube, it gives off water and becomes lighter. When heated in the air, it assumes a brick-red colour. It is infusible; is but little attacked by hydrochloric acid; dissolves easily in warm sulphuric acid. According to T. S. Hunt (Sill. Am. J. [2] ii. 30; also xi. 352), it contains —

$\text{TiO}_2$	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{Mg}_2\text{O}$	$\text{Ca}_2\text{O}$	$\text{H}_2\text{O}$
28.20	18.50	13.84	10.59	22.20	1.30	7.35 = 101.98;

whence Rammelsberg (*Mineralchemie*, p. 889) deduces the formula,



which by substituting  $al$  for  $\frac{2}{3}\text{Al}$ , may be reduced to  $2\text{M}^2(\text{Si} + \text{Ti})\text{O}^4 + al^2(\text{Si} + \text{Ti})\text{O}^4 + 2\text{aq.}$

Hunt and Dana regard the mineral as warwickite in a state of transformation. According to J. L. Smith (Sill. Am. J. [2] xvi. 293), it is a borotitanate of magnesium and iron, containing about 20 per cent. of boric anhydride.

**ENDELLIONITE.** Syn. with BOURNONITE.

**ENDIVE.** *Cichorium Endivia*.—This plant contains, according to Richardson (Ann. Ch. Pharm. lxvii. 377), 92.5 per cent. water, 6.1 organic substance, and 1.4 ash. The ash contains in 100 pts. 37.9  $\text{K}_2\text{O}$ , 12.1  $\text{Na}_2\text{O}$ , 12.0  $\text{Ca}_2\text{O}$ , 1.8  $\text{Mg}_2\text{O}$ , 5.2  $\text{SO}_3$ , 24.6  $\text{SiO}_2$ , and 6.4 phosphate of iron.

**ENDOMADERM.** Syn. with CHITIN.

**ENDOPHACIN.** The name given by Valenciennes and Fremy to the inner albuminous constituent of the crystalline lens of the eyes of mammalia.

**ENDOSMOSE.** See OSMOSE.

**ENGELHARDITE.** See ZIRCON.

**ENSTATITE.** A variety of augite,  $\text{Mg}^2\text{SiO}_3$ , found, together with pseudophite, on the Zdjär mountain near the Aloysthal, in Moravia. Forms firmly imbedded linear crystals, often transversely broken; they belong to the monoclinic system, exhibiting the faces  $[\alpha P\infty]$  and  $\alpha P\infty$  (the end-faces not developed), with distinct cleavage parallel to these faces and to those of a prism of nearly  $87^\circ$ . It is greyish-white, sometimes yellowish or greenish; dull on the faces of the crystal, but with a rather strong glassy and nacreous lustre on the cleavage-faces; semi-transparent or

translucent on the edges. Streak white. Brittle. Hardness = 5.5. Specific gravity = 3.10 to 3.13. Nearly infusible before the blowpipe, but becomes white and enamel-like on the edges: does not give any blue colouring with cobalt; insoluble in hydrochloric acid. Contains:—

SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O	Mg <sup>2</sup> O	H <sup>2</sup> O
56.91	2.50	2.76	55.44	1.92 = 99.53
57.28	. .	5.00	36.25	. . = 98.53

Of the water, 0.41 per cent. goes off at 100° C.; the rest at a red heat. (Kenngott, Wien. Akad. Ber. xvi. 162.)

**EOIDIN.** C<sup>2</sup>H<sup>4</sup>O<sup>3</sup>(?). A red colouring matter obtained from asparagus berries. (Kerndt, *Jahresber. d. Chem.* 849, 457.)

**EPHESITE.** A micaceous mineral, found, together with corundum, on the magnetic iron ore near Ephesus. It is laminar, easily separable in the direction of the laminae, white, nacreous, resembling white disthene. Specific gravity 3.15 to 3.20. Scratches glass easily. Before the blowpipe it becomes dull, but does not melt. Contains:—

SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	CaO	Fe <sup>2</sup> O	Na <sup>2</sup> O	H <sup>2</sup> O	Total
31.54	57.89	1.89	1.34	. .	3.12	. .
0.04	56.45	2.11	1.00	4.41	3.06	97.07

whence may be deduced the formula 2M<sup>2</sup>O.3SiO<sup>2</sup> + 2(2Al<sup>2</sup>O<sup>3</sup>.SiO<sup>2</sup>). (L. Smith, Ann. Min. [4] xviii. 294.)

**EPHESOMYDRIN.** See BROMHYDRINS (i. 667).

**EPICHLORHYDRIN.** See CHLORHYDRINS (i. 894).

**EPICHLORITE.** A mineral discovered by Zincken (Pogg. Ann. lxxvii. 237) near Neustadt in the Harz, where it occurs in a rock resembling serpentine, in fragments of radiating structure. It easily separates into prismatic forms, has a strong fatty lustre, dark leek-green colour, white streak inclining to greenish, and in thin slips is translucent, with bottle-green colour. Hardness = 2 to 2.5. Specific gravity = 2.76. Gives off water when heated in a tube, and melts with difficulty before the blowpipe. It is but imperfectly decomposed by hydrochloric acid. Contains:—

SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O	Mg <sup>2</sup> O	CaO	H <sup>2</sup> O
40.88	10.96	8.72	8.96	20.00	0.68	10.18

whence the formula 2(4M<sup>2</sup>O.3SiO<sup>2</sup>) + 2M<sup>2</sup>O<sup>3</sup>.3SiO<sup>2</sup> + 8 aq. (Rammelsberg, *Mineralchemie*, p. 539.)

**EPIDERMIS OF ANIMALS.** See HORNY TISSUE.

**EPIDERMIS OF PLANTS.** The skin of plants consists of one or more layers of compressed cellular tissue, constituting the true skin or epidermis, and of an external very thin layer of organic mucus, called the cuticle. The epidermis covers all parts of the plant which are exposed to the air, except the stigma, but is not found on plants habitually living under water. The cuticle covers every part except the openings through the stomates. According to Frey, the cellular substance of the epidermis consists of a peculiar substance, which he calls cutin, differing from ordinary cellulose in not being soluble in an ammoniacal solution of copper. Payen, on the other hand, regards the epidermis as consisting of ordinary cellulose impregnated with fats, nitrogenous bodies, and inorganic salts. (See CUTIN, p. 186.)

Mulder analysed the cuticle of *Agave Americana*, separated from the plant by maceration in sulphuric acid. After exhaustion with alcohol, ether, and water, and drying at 130° C. it left 4 per cent. of ash: the organic part contained 52.90 per cent. carbon, 6.79 hydrogen, and 40.31 oxygen and nitrogen. The substance was not, however, quite freed from epidermis cells, so that the result must be regarded as only approximate.

**EPIDERMOS.** See HORNY TISSUE.

**EPIDESMINE.** Syn. with EPISTILBITE.

**EPIDICHLORHYDRIN.** See CHLORHYDRINS (i. 894).

**EPIDOTE.** *Zoisite* (in part). *Pistacite*. *Thallite*. *Withamite*. *Akanticoon*. *Scorza*. *Delphinite*. *Arrendalite*. *Bucklandite*. *Thulite*. *Puschkinite*. *Achmantite*.

This mineral species, under the general formula 3(2M<sup>2</sup>O.SiO<sup>2</sup>) + 2(2R<sup>2</sup>O<sup>3</sup>.3SiO<sup>2</sup>) = 3M<sup>2</sup>SiO<sup>4</sup> + 2R<sup>2</sup>SiO<sup>3</sup>, or 3M<sup>2</sup>O.SiO<sup>2</sup> + 2(R<sup>2</sup>O<sup>3</sup>.SiO<sup>2</sup>), includes three sub-species, viz. 1. *Lime epidote* or *Zoisite* (in part) in which the monatomic metal M is almost wholly calcium, and the sesqui-atomic metal R is chiefly aluminium: this sub-species includes



*Thulite*.—2. *Lime and iron Epidote*, *Pistacite*, or *Epidote* proper, in which the calcium is sometimes partly replaced by iron (ferrosus), and the aluminium in great part by ferricum: this includes *Bucklandite* and *Puschkinite*.—3. *Manganesian epidote*, in which the sesquiatomic metal is partly manganese (manganicum). Besides these, must be mentioned *Allanite*, which is a true cerium epidote, and *Withamite*.

The crystals of epidote are monoclinic,  $a : b : c = 0.5509 : 1 : 0.9924$ . Inclination of principal axis to clinodiagonal =  $51^{\circ} 41'$ . Ordinary combination  $\infty P\infty + P\infty . -P\infty . [P\infty]$ . Cleavage most distinct parallel to  $+P\infty$ , less distinct parallel to  $\infty P\infty$ . Twin crystals occur, having their face of combination parallel to  $\infty P\infty$ . The crystals are always prismaticly elongated in the direction of the orthodiagonal. (Kopp, *Krystallographie*, p. 309.) Epidote likewise occurs columnar and granular, in particles of various sizes, sometimes impalpable.

Hardness = 6–7. Specific gravity = 3.25–3.5 (of zoisite, 3.2 to 3.45; of pistacite 3.35 to 3.5, of manganesian epidote 3.404; of withamite 3.1 to 3.34). Colour of zoisite grey or brown to white of pistacite, yellowish-green or pistachio-green, passing to olive and leek-green; of puschkinite, green, yellow, and red; of bucklandite, black; of manganesian epidote, reddish-brown, reddish, black or dark violet-blue; of withamite, bright red; of thulite, rose or peach-blossom red. Streak uncoloured, greyish or reddish. Subtransparent to opaque. Fracture uneven. Brittle.

Before the blowpipe, epidote melts on the edges and swells, but does not easily liquefy, the varieties containing most iron being the most fusible; borax-glass coloured by iron. The manganese variety fuses readily with intumescence, and gives with borax, an amethystine glass in the outer flame. Most specimens of epidote afford a minute globule of tin before the blowpipe. The specific gravity changes with heating. Epidote is but partially decomposed by acids, except after strong heating.

*Analyses*.—1. Brush (Sill. Am. J. [2] xxvi. 69).—2. Rammelsberg (*Mineralchemie*, p. 750).—3. Hermann (J. pr. Chem. xliii. 35).—4. Gmelin (Pogg. Ann. xix. 539).—5. Rammelsberg (*loc. cit.* 753).—6. Kühn (Ann. Ch. Pharm. lix. 373).—7, 8, 9. Hermann (*loc. cit.*)—10. Hartwell (Kongl. Vetensk. Acad. Handl. 1848, p. 171).—11. Sobrero (*loc. cit.* 1840, p. 218).—12. Geffken (*loc. cit.*)

#### I. *Lime Epidote.*

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sup>2</sup> O <sub>3</sub>	CaO	MgO	Loss by ignition	Na <sub>2</sub> O
1. Unionville, Pa. . .	40.61	33.44	0.49	24.13	. .	2.22	. . = 100.89
2. Sau alp . . .	40.64	28.39	3.89	24.26	0.57	2.09	. . = 99.84
3. Faltigl, grey . . .	40.95	30.34	5.51	21.56	. .	1.69	. . = 100.05
4. Thulite, Souland . .	42.84	31.14	2.29	18.73	1.64	0.64	1.89 = 99.13

#### II. *Lime and Iron Epidote.*

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sup>2</sup> O <sub>3</sub>	CaO	FeO	MgO	Na <sub>2</sub> O	Loss by ignition
5. Arendal . . .	37.98	20.78	17.24	23.74	. .	1.11	. .	. . = 100.85
6. Geier, Erzgeb. . .	40.57	14.47	13.44	30.00	. .	2.76	. .	. . = 101.24
7. Bourg d'Oisans . .	37.60	18.57	13.37	21.19	5.55	1.40	. .	1.68 = 98.36
8. Bucklandite . . .	36.97	21.84	10.19	21.14	9.19	. .	. .	1.00 = 100.33
9. Puschkinite . . .	37.47	18.64	14.15	22.06	2.56	. .	2.28	1.44 = 98.60

#### III. *Manganesian Epidote.*

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sup>2</sup> O <sub>3</sub>	Mn <sup>2</sup> O <sub>3</sub>	CaO	MgO	SnO.Cu <sub>2</sub> O
10. St. Marcel . . .	38.47	17.65	6.60	14.08	21.65	1.82	. . = 100.26
11. " . . .	37.86	16.30	8.23	24.45	13.42	. .	0.40 = 100.66
12. " . . .	36.87	11.76	10.34	18.25	22.78	. .	. . = 100.0

For other analyses see Rammelsberg, pp. 750–760; Dana, ii. 207).

The general formula  $3M'SiO^4 + 2R'SiO^{12}$ , deduced from these analyses, is composed of two terms, each of which represents an orthosilicate, and may be exhibited more plainly in that form by reducing the sesquioxides to protoxides, that is, by substituting in the second term of the formula,  $m = \frac{2}{3}R$ , which reduces that term to  $3m'SiO^4$ , and brings the entire formula to the general type  $M'SiO^4$ .

Epidotes occur in numerous localities. Fine crystals are found at Arendal in Norway: hence the name *Arendalite*. Other localities are the Ural, Piedmont, the Fichtelgebirg, Rothlaue in the Canton Berne, Faltigl in the Tyrol, Grossar in Austria, Bourg d'Oisans in Dauphiny, Glencoe, the mainland of Shetland, the Island of Icolmkill, &c. Epidote is of very frequent occurrence in primitive rocks, especially in granite, gneiss, and syenite. Iron epidote is, like garnet, a very frequent concomi-

tant of iron ores, especially of magnetic oxide; the numerous and extensive veins of this ore in Norway and Sweden are almost universally accompanied by these two minerals, especially in the neighbourhood of Arendal, where they almost displace the gneiss, which usually forms the matrix of the ore. The frequent occurrence of epidote and garnet in the same locality is easily explained by comparing the composition of the two minerals, garnet being  $3M'SiO^4 + R'Si^2O^{12}$ , and epidote  $3M'SiO^4 + 2R'Si^2O^{12}$ ; we may therefore suppose that in the formation of the older rocks, when ferroso-ferric oxide came in contact with silica, alumina and lime, epidote (especially pistacite) and garnet were produced, the former when the sesquioxides were present in greatest abundance, the latter when the protoxides predominated. (Scheerer, Handw. d. Chem. 1<sup>te</sup> Aufl. ii. 954.)

**EPIGLAUBITE.** A crystalline substance found in hardened guano, containing lime, phosphoric acid, and water. (Shepard, J. pr. Chem. lxx. 212.)

**EPSOMITE. EPSOM-SALT.** Sulphate of magnesium. (See SULPHATES.)

**EPISTILBITE.** A mineral belonging to the zeolite family, and closely allied to stilbite. Forms rhombic prisms with the acute lateral edges truncated. Fracture uneven. Hardness = 3·5 to 4. Specific gravity 2·249 to 2·263. White with glassy lustre, nacreous on the cleavage-faces. Dissolves in hydrochloric acid without gelatinising. Occurs in the almond-stone of Iceland and the Faroe Islands, and in the dolerite of Ireland. Gives by analysis 58·6 per cent. silica, 17·52 alumina, 7·56 lime, 1·78 soda, and 14·48 water: whence the formula,  $2Ca^2O \cdot 2Al^3O^3 \cdot 6SiO^2 + 10H^2O$ . =  $2Ca^2O \cdot 3SiO^2 + 2Al^3O^3 \cdot 3SiO^2 + 10H^2O$ . (G. Rose, *Gm. Handb.*, iii. 413; also Waltershausen, *Jahresber. d. Chem.*, 1853, 818; 1856, 863.)

**EQUATIONS, CHEMICAL.** See FORMULÆ.

**EQUISETIC ACID.** Syn. with ACONITIC ACID.

**EQUISETUM.** *Horse-tail.*—A genus of cryptogamous plants distinguished chemically by the large amount of inorganic constituents, especially silica, contained in them. The silica partly separates out on the external surface of the stem, where it hardens, forming numerous small concretions on the elevated striæ with which the stem is marked, and rendering it available for polishing substances of no great hardness, such as wood, ivory, horn, &c.

Braconnot found in 100 pts. of dried *Equisetum fluviatile*, 23·61 pts.; of *E. hiemale*, 11·81 pts.; of *E. arvense*, 13·84 pts.; and of *E. limosum*, 15·0 pts. ash consisting of:

	<i>E. fluviat.</i>	<i>E. hiem.</i>	<i>E. arvens.</i>	<i>E. limosum.</i>
Potash, partly as silicate . . . . .	0·72	0·30	trace	
Sulphate of potassium . . . . .	2·83	0·33	0·37	2·20
Chloride of potassium . . . . .	2·72	0·28	0·22	1·20
Carbonate of calcium . . . . .	1·46	0·93	5·51	1·50
Phosphate of calcium (containing iron) . . . . .	0·55	0·80	undeterm.	undeterm.
Sulphate of calcium . . . . .	3·39	. . .	. . .	3·30
Magnesia . . . . .	0·66	. . .	0·46	0·30
Silica . . . . .	12·00	8·75	6·38	6·50
	23·61	11·81	13·24	15·00

Witting (J. pr. Chem. lxi. 149) found in 100 pts. of *E. Telmateja* (a), dried at 100° C., 71·43 pts. organic substance, and 28·57 ash; in 100 pts. of the fresh plant of *E. arvense* (b), 78·45 water, 17·48 organic substance, and 4·07 ash. The ash contained in 100 pts.:

	SiO <sup>2</sup>	CO <sup>2</sup>	SO <sup>3</sup>	P <sup>2</sup> O <sup>5</sup>	Fe <sup>2</sup> O <sup>3</sup>	Mn <sup>2</sup> O	Mg <sup>2</sup> O	Mg <sup>2</sup> CO <sup>3</sup>	Ca <sup>2</sup> O	Ca <sup>2</sup> CO <sup>3</sup>	Na <sup>2</sup> O	K <sup>2</sup> O	NaCl	KCl
a . . . . .	66·15	0·49	2·65	1·28	1·83	0·12	0·62	2·24	2·11	10·67	0·003	1·23	1·12	9·92
b . . . . .	41·40	0·98	9·98	2·75	0·70	0·02	2·81	. . .	17·01	. . .	0·03	11·32	0·84	12·09

*E. arvense*, *E. hiemale*, and especially *E. palustre*, are said to be very injurious to cattle, whereas *E. fluviatile* forms a harmless and nutritious fodder. The various species of equisetum contain small quantities of equisetie (aconitic) acid in the form of calcium- or potassium-salt. Braconnot (*Ann. Ch. Phys.* [2] xxxix. 5) found in *E. limosum* a yellow colouring matter, which he designated as *flavequisetin* (q. v.)

**EQUIVALENTS.** No two substances in nature are absolutely equivalent in all respects, scarcely perhaps in any respect; but those are most nearly equivalent which manifest the greatest affinity to one another, either in regard to their general functions, or to some particular function taken as the criterion of resemblance. Now the prime indication of this special equivalency between two or more bodies is well known

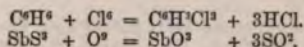
to consist in their capability of being freely exchanged for one another without loss or detriment; and this holds good no less in the science of chemistry than in the transactions of ordinary life, the idea of exchange, that is, of direct or indirect substitution, forming the basis of the modern doctrine of chemical equivalents.

We find in a great number of compounds that 1 pt. of hydrogen may be replaced directly by 23 pts. of sodium, or by 39 pts. of potassium, or by 108 pts. of silver, &c.; and as the resulting compounds manifest a marked mutual resemblance of constitution and properties, and a general resemblance to the hydrogenised body from which they were obtained, we say that the atoms of sodium, potassium, and silver are equivalent to one another, and also equivalent to an atom of hydrogen. Similarly, we find in a great number of compounds, both organic and inorganic, that one or more atoms of hydrogen may be replaced by an equal number of atoms of chlorine, or bromine, or iodine; and as the resulting compounds correspond closely with one another, and present a marked similitude to the original hydrogenised body, we say that the atoms of chlorine, bromine, and iodine are equivalent to one another, and also equivalent to an atom of hydrogen; whence it follows that the atoms of chlorine, bromine, iodine, hydrogen, potassium, sodium, and silver are mutually equivalent. We are acquainted with numerous bodies of comparable constitution, containing respectively an atom of chlorine or an atom of metal; thus:

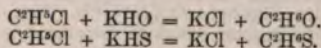
HHO .	Water	Cl <sup>s</sup> S .	Chlorine-sulphide
ClClO .	Hypochlorous anhydride	H <sup>s</sup> S .	Sulphydric acid
HClO .	Hypochlorous acid	Na <sup>s</sup> S .	Sodium-sulphide
KClO .	Hypochlorite of potassium	Cl <sup>s</sup> S <sup>2</sup> .	Chlorine-disulphide
KHO .	Hydrate of potassium	H <sup>s</sup> S <sup>2</sup> .	Hydrogen-disulphide
KKO .	Oxide of potassium	Na <sup>s</sup> S <sup>2</sup> .	Sodium-disulphide
C <sup>s</sup> H <sup>4</sup> Cl .	Ethyl-chloride	Cl <sup>s</sup> Sb .	Chlorostibine
C <sup>s</sup> H <sup>3</sup> H .	Ethyl-hydride	H <sup>s</sup> Sb .	Stibamine
C <sup>s</sup> H <sup>3</sup> Na .	Sodium-ethide	Ag <sup>s</sup> Sb .	Stibio-silver

That we are not acquainted with a very great number of such instances of replacement, appears to arise from the circumstance that, in few hydrogenised bodies can the hydrogen be replaced with equal facility by chlorine and by potassium. As a general rule, we find that the facility of replacement by potassium is directly, by chlorine inversely, as the degree of oxidation of the compound under examination, and consequently that the same body does not always afford both chlorine and metal derivatives. Chlorine and potassium are two elements possessing in the highest degree those opposite properties which we denominate chlorous and basylous respectively. They are, however, connected by a great number of intermediate links, and constitute, as it were, the extremities of a very long chain. From the antagonism in properties possessed by chlorous and basylous elements, we find that the correspondence in properties between chlorous and basylous derivatives of the same hydrogenised body is confined within narrow limits; it is, however, well manifested in the phenomena of double decomposition.

We may make a similar comparison between other elements than those which we have as yet considered. Thus in a whole host of most varied bodies, we find that 16 pts., or 1 atomic proportion of oxygen, are replaceable by 32 pts., or 1 atomic proportion of sulphur; and that the comparable oxygen and sulphur compounds are either procurable from one another by an atomic exchange of oxygen for sulphur, or may be obtained by precisely similar reactions from oxygen and sulphur respectively. Just, for instance, as chlorine expels hydrogen from benzene, so does oxygen expel sulphur from stibnite:



Carbon burns in oxygen gas to form the dinoxide CO<sup>2</sup>, and in sulphur-vapour to form the disulphide CS<sup>2</sup>. Again, the analogous bodies, alcohol and mercaptan, are procurable from hydrochloric ether by means of hydrate and sulphydric acid of potassium respectively, thus:



In a similar manner we may compare together the elements phosphorus, arsenic, antimony, and bismuth, when we shall find that their respective atoms are mutually interchangeable, and consequently equivalent one to another.

In the different instances of equivalent substitution above referred to, the replacement has been effected by an interchange of atom for atom; but we constantly find in addition, that two, three, or more atoms of one element may be exchanged for one



atom of another. Thus, if we act upon pentachloride and pentabromide of phosphorus with water and sulphydric acid respectively, we have the following reactions:—



In these reactions, as in very many others, we find that two atoms of chlorine and bromine are respectively exchangeable for one atom of oxygen or sulphur. Hence, taking the atom of hydrogen as the unit of equivalency, we say that the atoms of chlorine and bromine have a single, and the atoms of oxygen and sulphur a twofold equivalency. Again, if we take three atoms of hydrochloric acid,  $\text{H}^3\text{Cl}^3$ , we can either displace the three atoms of hydrogen by three atoms of sodium, to form three atoms of chloride of sodium,  $\text{Na}^3\text{Cl}^3$ , or we can displace them by one atom of bismuth to form one atom of trichloride of bismuth,  $\text{BiCl}^3$ ; so that while the atom of sodium has a single, the atom of bismuth has a threefold equivalency, the one atom of bismuth being a representative of three atoms of hydrogen or of sodium. To facilitate comparison, the author of this article proposed, some few years back, that mode of indicating differences in equivalent value which has now come into very general use—namely, by means of one or more dashes placed to the right of the symbols, so as to establish a difference to the eye between the equivalent or substitution values of different atoms, as shown in the following formulæ:—

$\text{AgCl}^1$	.	.	Silver chloride	$\text{AgPO}^4$	.	Silver phosphate
$\text{Sn}^{\text{''}}\text{Cl}^2$	.	.	Stannous chloride	$\text{HSn}^{\text{''}}\text{PO}^4$	.	Stannous phosphate
$\text{Bi}^{\text{'''}}\text{Cl}^3$	.	.	Bismuth chloride	$\text{Bi}^{\text{'''}}\text{PO}^4$	.	Bismuth phosphate

It is observable that the equivalency of an elementary atom referred to that of hydrogen as unity, may be determined almost equally well by noticing the number of chlorine-, or hydrogen-, or sodium-atoms, with which it can unite, as by noticing the number of chlorine-, or hydrogen-, or sodium-atoms which it can replace. For every combination of an element with chlorine may be looked upon as a substitution-product of chloride of sodium, in which a certain number of sodium-atoms are replaced; and every combination of an element with sodium as a substitution-product of chloride of sodium, in which a certain number of chlorine-atoms are replaced. Trichloride of bismuth,  $\text{Bi}^{\text{'''}}\text{Cl}^3$  for instance, is derivable from three atoms of chloride of sodium,  $\text{Na}^1\text{Cl}^1$ , by a displacement of three uniequivalent atoms of sodium by one triequivalent atom of bismuth; while sulphide of sodium,  $\text{Na}^2\text{S}^1$ , is derivable from two atoms of chloride of sodium,  $\text{Na}^1\text{Cl}^1$ , by an exchange of two uniequivalent atoms of chlorine for one dis-equivalent atom of sulphur, &c. &c.

In modern chemistry, the notion of equivalency is usually extended to that of interchangeable value for hydrogen or for the representatives of hydrogen, as above explained, irrespective of any similarity or dissimilarity in properties between the equivalent bodies. In this broad sense, an atom of oxygen  $\text{O}^2$  is equivalent, not only to an atom of its analogue, sulphur  $\text{S}^2$ , but also to an atom of its heterologue, tin  $\text{Sn}^4$ ; while the atom of antimony,  $\text{Sb}^3$ , is equivalent, not only to the respective atoms of its analogues, arsenic  $\text{As}^3$  and bismuth  $\text{Bi}^3$ , but also to the respective atoms of its heterologues, boron  $\text{B}^3$ , and gold  $\text{Au}^3$ . Again, six atoms of hydrogen  $6\text{H}^1$ , three atoms of sulphur  $3\text{S}^2$ , and two atoms of gold  $2\text{Au}^3$ , constitute equivalent quantities of the three highly dissimilar elements.

This idea of equivalency is widely removed from that of atomicity, and is indeed quite compatible with the notion of fractional proportions. There is no impropriety, for instance, in saying that an atom of hydrogen is equivalent to one-half an atom of tin or sulphur, and to one-third of an atom of bismuth or phosphorus. This mode of expression is associated, moreover, with the use of a special equivalent notation, as distinguished from the atomic notation commonly employed. In this equivalent notation, introduced by Laurent and Gerhardt, the proportions of the different elements which are exchangeable for one atom of hydrogen are represented by the same letters which symbolise their respective atoms, but written in small letters only instead of with capitals, thus:—

$\text{HCl}^1$	Hydrochloric acid	$\text{HCl}^1$
$\text{NaCl}^1$	Sodium-chloride	$\text{NaCl}^1$
$\text{S}^{\text{''}}\text{Cl}^2$	Sulphur-chloride	$\text{s}^{\text{''}}\text{Cl}^2$
$\text{Sn}^{\text{''}}\text{Cl}^2$	Stannous-chloride	$\text{sn}^{\text{''}}\text{Cl}^2$
$\text{P}^{\text{''}}\text{Cl}^2$	Phosphorous-chloride	$\text{p}^{\text{''}}\text{Cl}^2$
$\text{Bi}^{\text{'''}}\text{Cl}^3$	Bismuth-chloride	$\text{bi}^{\text{'''}}\text{Cl}^3$
$\text{C}^{\text{''''}}\text{Cl}^4$	Carbon-chloride	$\text{c}^{\text{''''}}\text{Cl}^4$
$\text{Si}^{\text{''''}}\text{Cl}^4$	Silicon-chloride	$\text{si}^{\text{''''}}\text{Cl}^4$





very commendable, if used merely to represent equivalent quantities, but they cannot be correctly used to represent the atoms of the elements or their smallest indivisible combining proportions; indeed, Gerhardt himself, after he had begun to employ the multiequivalent compound radicles presently to be described, was more and more disposed to regard his symbols as mere expressions of equivalent quantities and not of atomic weights.

The doctrine of equivalency is not by any means confined to elementary bodies, but is applicable to all the varieties of compounds, real or hypothetical, with which chemists are acquainted, and more particularly to those groupings which are denominated compound radicles. Whether or not we admit the independent existence of preformed compound radicles, it is indisputable that certain groupings of atoms are capable of being transferred from one combination to another in exchange for an atom of hydrogen, or chlorine, or metal; or in other words, are capable of replacing hydrogen, chlorine, or metal by equivalent substitution. Thus we can transfer the molecular groupings which we denominate cyanogen,  $CN$ ; amidogen,  $NH^2$ ; peroxide of hydrogen,  $HO$ ; benzoyl,  $C^6H^5O$ ; acetyl,  $C^2H^3O$ ; ethyl,  $C^2H^5$ ; amyl,  $C^5H^{11}$ , &c., from one compound to another, in exchange for one another, or for hydrogen, or its representatives, with a facility by no means inferior to that with which we effect actual elementary substitutions; and for a long time past these groupings have been looked upon as the representatives or equivalents of one atom of hydrogen. But the notion of multiequivalency, in relation to compound radicles, is much more recent, it having been first announced by Williamson in 1851, and then not as a consequence, but as an anticipation, of its already described application to several of the basylous metals, which was first advocated by the author of this article in 1854-55. Just as we can exchange an atom of ethyl ( $C^2H^5$ ) or cyanogen ( $CN$ ) for one atom of hydrogen, so can we exchange an atom of sulphuryl ( $SO^2$ ) or carbonyl ( $CO$ ) or oxalyl ( $C^2O^2$ ) or ethylene ( $C^2H^4$ ) for two atoms of hydrogen, and an atom of phosphoryl ( $PO$ ) or glyceryl ( $C^3H^5$ ) for three atoms of hydrogen, &c. &c.

A multiequivalent radicle, whether elementary or compound, is characterised by the property of combining several atoms or residues into one more complex atom, and is hence spoken of as polyatomic, the multiequivalency or polyatomicity of radicles being indeed one and the same function, looked at from a somewhat different point of view. Comparing chloride of bismuth,  $BiCl^3$ , with chloride of hydrogen,  $3HCl$ , for instance, the atom of bismuth is triequivalent, inasmuch as it displaces three atoms of hydrogen, and it is triatomic, inasmuch as it unites the three chlorine residues into one complex atom or molecule. Again, the diequivalent radicles, ethylene,  $C^2H^4$ , and sulphuryl,  $SO^2$ , by their substitution for hydrogen, bind together the residues of two atoms of hydrochloric acid, of two atoms of water, of two atoms of ammonia, &c. &c., and are consequently diatomic. Thus we have  $(C^2H^4)Cl^2$  and  $(SO^2)Cl^2$  comparable with  $2HCl$ ,  $(C^2H^4)H^2O^2$  and  $(SO^2)H^2O^2$  comparable with  $2H^2O$ , and  $(C^2H^4)H^4N^2$  and  $(SO^2)H^4N^2$  comparable with  $2H^4N$ .

By referring to the article CLASSIFICATION, it will be seen that in every definite molecule the sum of the equivalencies or atomicities of the constituent radicles, whether elementary or compound, is always an even number, and that the equivalency or atomicity of a radicle increases by one unit for every atom of hydrogen or hydrogen-substitute abstracted from the molecule. In the case of marsh-gas,  $CH^4$ , for instance, by abstracting  $H^1$  we have the unequivalent radicle *methyl* ( $CH^3$ ), which combines with one atom of chlorine to form chloride of methyl,  $(CH^3)Cl$ ; by abstracting  $H^2$  we have the diequivalent radicle *methylene* ( $CH^2$ ), which combines with two atoms of chlorine to form dichloride of methylene,  $(CH^2)Cl^2$ ; by abstracting  $H^3$  we have the triequivalent radicle *formyl* ( $CH$ ), which unites with three atoms of chlorine to form trichloride of formyl,  $(CH)Cl^3$ ; and, lastly, by abstracting  $H^4$  we have the tetrequivalent radicle *carbon*  $C$ , which combines with four atoms of chlorine to form tetra-

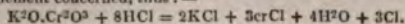
Similarly, the smallest proportion of platinum that can enter into a combination has the same weight, and not one-half the weight, of an atom of platinum. By reducing all chlorides and oxides to protochlorides and protoxides, we ignore the following facts:—

1. That there is a great distinction in properties between protosalts and di- or sesqui-salts. Aluminium, for instance, forms but one set of salts: these might very well be considered as protosalts, but they are not so considered, simply because their properties are altogether different from those of protosalts.

2. That in well-defined molecules, we rarely find so small a quantity of platinum, or of ferric, as corresponds with Gerhardt's atomic weights, but twice the former, and three times the latter quantity, thus:—

Hydrochlorate of platinamine	$HCl.NHpt^2$	Iron-alum	$fe^3K(SO^4)^2$
Hydrochlorate of diplatinamine	$HCl.N^2H^2pt^2$	Magnetic oxide of iron	$fe^3FeO^2$
Ammonio-chloride of platinum	$NH^4Cl.pt^2Cl^2$		

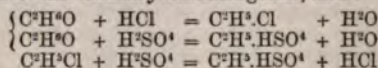
3. That twice pt and three times fe, cr, al, &c., are usually the smallest quantities of pt and fe, &c., that can result from, or effect, those reactions in which the reacting quantities are determined by the amount of some other element concerned, thus:—



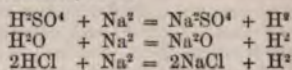


chloride of carbon,  $C^{''' }Cl^4$ . Again, it will be often found that the same radicle has, and must have, two or more distinct equivalencies or atomicities. Thus the radicle  $C^2H^2$ , when resulting from the dehydrogenation of tritylene,  $C^2H^2$ , is uniequivalent or monatomic, and unites with one atom of chlorine to form chloride of allyl,  $(C^2H^2)Cl$ ; but when resulting from the dehydrogenation of hydride of trityl,  $C^2H^2$ , it is triequivalent or triatomic, and unites with three atoms of chlorine to form trichloride of glyceryl,  $(C^2H^2)Cl^3$ . But how it is that these relations subsist, and why it is that they must subsist, have been already fully considered in the article on CLASSIFICATION, above referred to.

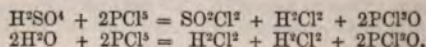
The notion of equivalency, hitherto exemplified in its application to elementary and compound radicles, may likewise be extended to molecules, though with a less degree of precision. Thus every molecule containing a displaceable atom of hydrogen, or the representative of a displaced atom of hydrogen, is in one sense equivalent to a molecule of hydrochloric acid,  $HCl$ , or to the double atom of hydrogen,  $H^2$ ; but in another sense it may be equivalent to very many such molecules or double atoms. For instance, a molecule of water,  $H^2O$ , is in one sense equivalent to a molecule of hydrochloric acid,  $HCl$ . Both molecules, when treated with metallic sodium, lose an atom of hydrogen in exchange for an atom of sodium, which remains combined with the residues,  $Cl$  and  $HO$  respectively, which residues are capable of being freely exchanged for and are consequently equivalent to one another; as in the following example:—  
 $NO.Cl + Na.HO = NO.HO + Na.Cl$ ,—so that we have  $H^2$  equivalent to  $HCl$ , equivalent to  $H^2O$ . Again, the molecule of sulphuric acid,  $H^2SO^4$ , is equivalent to a molecule of hydrochloric acid or of water; for we are acquainted with scores of instances in which the molecules  $HCl$  and  $H^2SO^4$  effect precisely similar reactions, or in which the residues  $Cl$  and  $HSO^4$  are mutually interchangeable, thus:



But in other cases we find the molecules of water and sulphuric acid equivalent to two molecules of hydrochloric acid, thus:



Moreover, though in the above instances the molecules of sulphuric acid and water are equivalent to one another, yet in other instances one molecule of sulphuric acid is equivalent to two molecules of water, thus:—



Or the molecule of hydrochloric acid being equivalent to two atoms of hydrogen, the molecule of water is equivalent sometimes to two, sometimes to four, atoms of hydrogen, and the molecule of sulphuric acid to two, four, six, or eight atoms, &c. We have already seen that marsh gas, regarded as hydride of methyl,  $CH^3.H$ , is equivalent to two atoms of hydrogen; but regarded as dihydride of methylene,  $CH^2.H^2$ , it is equivalent to four atoms of hydrogen; regarded as trihydride of formyl,  $CH.H^3$ , it is equivalent to six atoms of hydrogen; while regarded as tetrahydride of carbon,  $C^{''' }H^4$ , it is equivalent to eight atoms of hydrogen. We thus arrive at the conclusion, that the maximum equivalency of any molecule is the sum of the equivalencies of its constituent atoms, whilst its minimum equivalency is that of the most simple type to which it can be referred. Generally speaking, however, when comparing the equivalencies of more or less similarly functioned bodies, we consider them to be formulated upon those types with which their most characteristic reactions correspond. Thus, although every dibasic acid is of necessity monobasic also, and capable of undergoing a whole series of reactions, and producing a whole series of compounds, which are strictly comparable to those of an undoubted monobasic acid, yet we seldom refer it to a monatomic type, but remember only its more characteristic dibasic habitudes, and represent its equivalency as double that of a monobasic acid. For example, we do not usually accord to sulphuric acid the formula  $H(HSO^4)$  comparable with  $HCl$ , and equivalent to two hydrogen-atoms, but rather the formula  $H^2(SO^4)$  comparable with  $2HCl$ , and equivalent to four hydrogen-atoms, and so in other instances. W. O.

**ERBIUM.** The metallic radicle of erbia, one of the earths associated with yttria. Its atomic weight has not been determined.

Erbia was discovered in 1843, by Mosander (Ann. Ch. Pharm. xlviii. 219); its name is derived from Ytterby, the locality of gadolinite, in which mineral erbia occurs

together with yttria and terbia. These three earths, which were formerly confounded together under the general name yttria, differ from one another in basic power, erbia being the weakest; but no complete method of separating them has yet been discovered. A partial separation is effected by fractional precipitation with caustic ammonia from the solution of the nitrates, or with acid oxalate of potassium from that of the sulphates, erbia going down first, then terbia, and lastly yttria. (See Yttrium).

Erbia, obtained by igniting the precipitated hydrate, has a deep yellow colour; when prepared by igniting the oxalate or the nitrate, it is lighter in colour, probably on account of finer mechanical division. When ignited in hydrogen gas, it yields a small quantity of water, and becomes colourless. It dissolves in hydrochloric acid without perceptible evolution of chlorine. The solutions of its salts are colourless. The sulphate has a sweetish taste, and crystallises like sulphate of terbia (*q. v.*), but is distinguished therefrom by not efflorescing at 80° C., even when kept at that temperature for a week. The solution of the nitrate does not become coloured when concentrated; and the salt, which forms radiating crystals, often colourless, but sometimes with a reddish tinge, does not deliquesce; in both these respects, it differs from sulphate of terbia.

**EREMACAUISIS or Decay.** A slow combustion taking place in presence of air and water, and accompanied by a kind of fermentation. The water doubtless acts in this process in the same manner as in the rusting of iron, viz. by absorbing the oxygen of the air, and transferring it in the liquid form to the constituents of the organic compound. Simple oxidation of organic substances in the air, such as the conversion of aldehyde into acetic acid, or the resinifying of volatile oils by exposure to the air, are not generally regarded as instances of eremacausis.

In eremacausis or decay, the carbon and hydrogen of the compound are converted by combustion into carbonic acid and water, while the nitrogen either escapes in the form of gas, or is converted into nitrous and nitric acid. As in this process the compound continually loses more and more carbon and hydrogen, it might be supposed that the residue would become continually richer in oxygen. This, however, is not always the case. For while the carbon of the compound is combining with the oxygen of the air and forming carbonic acid, it is possible that a large portion of the oxygen contained in the compound may go off with the hydrogen in the form of water, so that the residue may become richer in carbon than the original compound. Such, according to Saussure, is the process which takes place in the decay of wood, and its conversion into humus or mould, a substance which is richer in carbon, but is afterwards, by a further process of decay, completely converted into carbonic acid and water.

A decaying substance may bring other bodies into the state of slow combustion. Decaying organic substances surrounded with a mixture of hydrogen gas and air or oxygen, cause it to condense in the form of water (Saussure). Decaying substances in contact with water and alcohol cause the latter substance to oxidise and form acetic acid. (Liebig.)

Eremacausis is accompanied by evolution of *heat*; which in most cases, in consequence of the slowness with which it takes place, and the cooling produced by surrounding objects, amounts to only a few degrees, but when large masses are concerned, may, under favourable circumstances, rise to such a height as to induce rapid combustion (see COMBUSTION, i. 1093). In some few cases, eremacausis is attended with development of *light*, as in decaying wood, &c.

With regard to the behaviour of nitrogen in eremacausis, a great number of particulars have to be observed.

1. The nitrogen of an organic compound escapes in the form of gas, especially if the air has free access, or the compound is exposed to the sun, and no salifiable bases are present.

2. It is converted into nitric acid, especially with free access of air, in the shade, and in presence of a salifiable base, which favours the formation of the nitric acid. This base may be potash, soda, lime, or magnesia, in combination with carbonic acid or a vegetable acid: for the carbonic acid escapes as fast as the nitric acid comes in contact with the potash, and the organic acid is destroyed by the slow combustion. The ammonia produced by fermentation in the interior of the mass may also, when it reaches the surface, induce the oxidation of the nitrogen which is there being set free, and form nitrate of ammonia by combining with it, as was formerly observed by Thaer and Einhof, in the putrefaction of cow-dung. If fixed salifiable bases are present, the nitrogen of the ammonia itself may also be oxidised and converted into nitric acid. (Kühlmann.) According to Vaudin's experiments, the formation of nitric acid appears to be preceded by that of nitrous acid.

3. The nitrogen of the compound unites with its hydrogen, and forms ammonia, which generally escapes as carbonate. This ammonia is not so much a product of eremacausis as of fermentation.



4. Non-azotised organic compounds appear, under certain circumstances, to absorb nitrogen from the air during eremacausis, either in the form of ammonia or of nitrous acid.

Extract of *Hyoscyamus*, when kept for a long time, forms carbonate of ammonia in the interior of its mass, but becomes covered on the surface with needles of nitrate of ammonia. (Flaschoff.)

The leaves of mangoldwurzel, grown on a poor, sandy soil, do not contain any perceptible quantity of nitre (those which grow on a rich soil contain a considerable quantity), but chiefly malate and oxalate of potassium. But when suspended on threads for some months, they become thoroughly penetrated with nitre and covered with fine crystals, nitric acid having, in fact, been formed by decomposition of the azotised matter in the leaves; the oxalate and malate are found to have disappeared entirely. (Braconnot, Ann. Ch. Phys. xxxv. 261; also Pogg. Ann. x. 506.)

Extract of quassia, after a year's exposure to the air, contains more nitre than it would contain if kept for the same time in close vessels. (Planche, J. Pharm. xxiii. 548.)

Extract of *Borago officinalis*, when not sufficiently evaporated, gives off nitric oxide gas on being stirred. (Guibourt, J. Pharm. xii. 134.)

The aqueous infusion of orange leaves evaporated in the air on flat dishes, yields, according to Vaudin, an extract, which, if exposed for a few hours to damp air, and then collected in a pot, swells up considerably, from evolution of nitrous acid, and continues for some months to give off this gas, whenever it is stirred.

It appears to be the woody fibre of plants which more especially attracts the nitrogen of the air; and the nitrogen thus absorbed takes up oxygen and remains combined with the woody fibre in the form of nitrous acid, till that acid is transformed into nitric acid, which then unites with the potash and lime contained in the salts of the vegetable acids present. When liquorice-wood is exhausted 22 times, first with cold, and then with hot water, the last extract still gives off nitrous fumes when treated with tartaric acid. The juice expressed from the fresh herb of *Lycopsis arvensis* contains neither nitrous acid nor nitre: but the exhausted residue, after four weeks' exposure to the air, yields with hot water an extract which gives off nitrous acid when treated with tartaric acid, and deflagrates on red-hot coals. When Iceland moss (*Lichen islandicus*) is several times exhausted, first with cold and then with hot water, and exposed to the air for some time after each immersion, all the extracts yield nitrous acid and nitre. (Vaudin, J. Chim. méd. i. 674; ix. 321.)

When the air has but partial access, part of the hydrogen of the organic compound appears to combine with the nitrogen of the air and form ammonia, which can then supply the requisite quantity of nitrogen to the fungi which grow upon these putrefying substances.

When an aqueous solution of milk-sugar or common sugar is left for three months in a stoppered bottle, together with a sevenfold volume of air, and the mould, which is produced in particular abundance from the milk-sugar, is subjected to dry distillation, a large quantity of ammonia is obtained; hence there has been produced in the fungus, together with cellulose, a nitrogenous substance, doubtless of albuminous nature; for when the fungus produced from milk-sugar is digested in acetic acid, a liquid is obtained which gives a precipitate with ferrocyanide of potassium. Starch from arrow-root, when kept under water in a bottle also containing air, soon becomes very turbid, and in ten weeks forms a white deposit, together with a large quantity of mould in the mass, and finally also a little on the surface. A fungus of this kind obtained from potato-starch yielded strong traces of ammonia when subjected to dry distillation. A mixture of humic acid and sugar, moistened with a small quantity of water, and kept for six months in a closed vessel containing air, gives off a large quantity of ammonia when treated with potash. In a similar manner, woody fibre, which putrefies with scanty access of air in the lower strata of a vegetable soil, appears to form ammonia, part of the hydrogen of the wood combining with the oxygen of the air, and another portion with the nitrogen. This ammonia, according to Kühlmann's supposition, may be afterwards transformed into nitric acid. In this manner we might explain the formation of nitre in the caves of Zeilan described by J. Davy, where no animal substances can be discovered [there are, however, nitrogenous vegetable matters present]; also the formation of nitre in India, Spain, Egypt, in the grottoes on the banks of the Seine, and in many cellars. (Mulder, J. pr. Chem. xxxii. 326, 344.)

Damp wood, putrefying in confined air, converts the oxygen of the air into an equal volume of carbonic anhydride, producing, at the same time, much more water than carbonic anhydride (Saussure). At the same time, however, a small quantity of nitrogen is absorbed from the air, and some of it is converted into ammonia, while



the remainder enters as nitrogen into the composition of certain fungoid substances, which are formed at the same time. (Hermann, J. pr. Chem. xxvii. 166.)

Many organic compounds do not undergo slow combustion at ordinary temperatures or in the dark, but exhibit that phenomenon when moderately heated or exposed to light, especially to direct sunshine.

Air is necessary as well as heat; substances which, between 100° and 120° C., suffer no alteration out of contact of air, decompose in the air, even when but slightly heated. (Chevreul, *Analyse Organique*, p. 69.)

Compounds which remain unaltered when exposed to the air at medium temperatures in the dark, become changed when likewise exposed to light. These changes, due to the action of light, are especially conspicuous in many organic colouring matters, such as indigo, prussian blue, safflower, turmeric, and the colours of many flowers which are bleached thereby. (Chevreul.)

Coloured fabrics, e.g. silk and wool dyed with safflower, weld, or turmeric, which gradually fade on exposure to sunlight, suffer the same change in an hour or two, when subjected in the dark to a heat between 160° and 200° C., the air having access to them at the same time. (Gay-Lussac and Thénard, *Recherches physico-chimiques*, ii. 166; Gm. vii. 96.)

**ERDMANNITE.** A silicate containing cerium (perhaps an impure orthite), from the island of Stokö, near Brevig, Norway, where it occurs in dark brown, translucent, imbedded grains and folia, with no traces of crystallisation. Lustre vitreous. Specific gravity 3·1. According to a preliminary analysis by Blömstrand (Pogg. Ann. lxxxvii. 168), it contains 31·35 per cent. silica, 34·89 oxides of cerium and lanthanum, 11·71 alumina, 6·46 lime, 8·52 ferrous oxide, 0·86 manganous oxide, 1·48 yttria, 4·28 water and loss.

**EREMITE.** The name given by Shepard (Sill. Am. J. xxxii. 341; xxxiii. 70) to a ceriferous mineral, which, according to Berzelius, is perhaps fluocerite, but is regarded by Dana as monazite (*q. v.*), although, according to Shepard, it contains fluorine.

**ERGOTINE.** The active principle of ergot of rye. It is obtained by treating the ergot with ether to remove fatty and waxy matters, digesting the residue in boiling alcohol, concentrating the solution by evaporation, and precipitating by cold water. It is a red-brown powder, having a sharp bitter taste, infusible, insoluble in water, ether, and dilute acids, soluble in alcohol, strong acetic acid, and caustic potash; sulphuric acid dissolves it with red-brown colour. Its action on the animal economy is said to be slowly but mortally narcotic. (Wiggers, Ann. Ch. Pharm. i. 171.)

**ERICA CARNEA.** This plant, grown on a magnesian limestone soil, and gathered in June, gave off 48·75 per cent. water, at 100° C., and the dry residue yielded 2·66 ash, containing 21·95 per cent. K<sup>2</sup>O, 1·46 Na<sup>2</sup>O, 32·07 Ca<sup>2</sup>O, 14·28 Mg<sup>2</sup>O, 3·44 Fe<sup>2</sup>O<sup>3</sup>, trace of manganic oxide, 5·43 P<sup>2</sup>O<sup>5</sup>, 5·44 SO<sup>3</sup>, 3·57 NaCl, and 12·38 silica. (Röthe, Ann. Ch. Pharm. lxxxvii. 118.)

**ERICA VULGARIS.** Syn. with *CALLUNA VULGARIS* (i. 722).

**ERICACEÆ.** According to Rochleder (Ann. Ch. Pharm. lxxxiv. 368) all plants of this order contain tannic acids, the anhydrides of which may be represented by the general formula C<sup>14</sup>H<sup>12</sup>O<sup>8</sup>, e. g.

Gallic acid	C <sup>14</sup> H <sup>12</sup> O <sup>10</sup> in <i>Arctostaphylos uva ursi</i>
Callutannic acid	C <sup>14</sup> H <sup>12</sup> O <sup>8</sup> „ <i>Calluna vulgaris</i>
Rhodotannic acid	C <sup>14</sup> H <sup>12</sup> O <sup>7</sup> „ <i>Rhododendron ferrugineum</i>
Leditannic acid	C <sup>14</sup> H <sup>12</sup> O <sup>6</sup> „ <i>Ledum palustre</i>

and according to Kuberth's investigations (*loc. cit.*) *Erica herbacea* contains a similar acid, the anhydride of which is C<sup>14</sup>H<sup>12</sup>O<sup>7</sup>. All these acids (excepting gallic acid) turn ferric salts green, form a yellow precipitate with stannic chloride, and, when heated with sulphuric or hydrochloric acid, give up the elements of water, and form a yellow or red colouring matter. They all contain ericolin, a volatile oil, and probably also small quantities of citric acid (Rochleder). According to Uloth (Ann. Ch. Pharm. cxi. 216) all ericaceous plants yield, by dry distillation, a crystallisable substance called ericinone.

**ERICINOL.** C<sup>14</sup>H<sup>14</sup>O. A product of the decomposition of ericolin (p. 500) and of pinipicrin, obtained, together with glucose, by distilling either of those substances with dilute sulphuric or hydrochloric acid. It then passes over as a volatile oil, colourless at first, but sooner turning brown, from oxidation (Rochleder, Schwarz, and Kawalier). Its formation from ericolin is represented by the

equation,  $C^{10}H^{16}O^{21} + 4H^2O = 4C^8H^{12}O^8 + C^{10}H^{16}O$ ; and from pinipicrin, by  $C^{22}H^{36}O^{11} + 2H^2O = 2C^8H^{12}O^8 + C^{10}H^{16}O$ .

The same volatile oil, but already somewhat altered, is obtained by distilling with water the leaves of *Calluna vulgaris*, *Rhododendron ferrugineum* (Rochleder), *Arctostaphylos uva ursi* (Kawaler), *Ledum palustre* (Willigk), and *Erica herbacea* (Kuberth).

The volatile oil of *Ledum palustre* is a mixture of ericinol with valeric acid, another oily acid, and an oil isomeric with oil of turpentine, boiling at  $160^{\circ}$  C. When freed from the acids by repeated agitation with potash-ley, then washed and dehydrated, it yields by distillation between  $115^{\circ}$  and  $160^{\circ}$  C. a mixture of ericinol and non-oxygenated oil, but between  $236^{\circ}$  and  $250^{\circ}$ , chiefly ericinol, while a resin remains behind.

Ericinol thus obtained is a bluish green oil, having a disagreeable smell, and burning, nauseously bitter taste, and boiling between  $240^{\circ}$  and  $242^{\circ}$  C. When once distilled with sticks of potash, it is partially discoloured, has a specific gravity of 0.874 at  $20^{\circ}$ , and contains on the average 79.96 per cent. carbon and 11.03 hydrogen, agreeing approximately with a formula  $C^{10}H^{16}O$  (calc. 78.96 C and 10.62 H). By cobobation with excess of solid potash, it is converted into a non-oxygenated oil,  $C^{10}H^{16}$  (Fröhde, J. pr. Chem. lxxxii. 181).

**ERICINONE.**  $C^{24}H^{40}O^9$  (?) (Uloth, Ann. Ch. Pharm. cxi. 215.) An indifferent crystalline substance, obtained by the dry distillation of ericaceous plants. On submitting the extract of a plant of this order to dry distillation, and precipitating the liquid distillate with acetate of lead, ericinone remains dissolved, and may be obtained in the crystalline form by precipitating the lead with sulphydric acid, evaporating the filtrate to dryness, and subliming the residue between two watch-glasses in small quantities at a time.

Pure ericinone sublimes in feathery groups of white crystals having a silky lustre. It dissolves easily in alcohol and ether, and crystallises from the alcoholic solution in quadratic needles, acuminate with triangular or rhombic faces. Its solution, when fresh, is neutral to vegetable colours, but decomposes gradually, turning brown and acquiring an acid reaction: the crystals likewise undergo slow alteration, especially under the influence of light. Ericinone is inodorous, but has a sweetish taste, with somewhat astringent after-taste. It melts at about  $167^{\circ}$  C., and solidifies in the crystalline state. Sublimation begins far below the melting point; at higher temperatures it is attended with partial carbonisation.

The solution of ericinone is not precipitated by acetate of lead, either neutral or basic, but on addition of ammonia a white precipitate is formed, which afterwards becomes dark-coloured. It is not altered by ferrous or ferric salts: it quickly reduces silver and gold from their salts; platinum from the chloride on addition of ammonia, and boiling; cuprous oxide from an alkaline cupric solution, even in the cold. In contact with alkalis, it quickly turns brown and absorbs oxygen, the colour disappearing, however, as soon as all the ericinone is decomposed.

Nitric acid converts ericinone into oxalic acid. Hydrochloric acid dissolves it without decomposition; but on adding chlorate of potassium to the warm solution, chloranil,  $C^6Cl^2O^2$ , separates out.

According to Uloth's analyses, ericinone contains 62.85—63.40 per cent. carbon and 5.48—5.26 hydrogen, whence he deduces the formula  $C^{24}H^{40}O^9$  or  $C^{22}H^{36}O^9$  (calc. 63.16 carbon and 5.26 hydrogen). He thinks it probable that ericinone is a product of the decomposition of ericolin. Hesse (Ann. Ch. Pharm. cxiv. 301) regards ericinone as identical with hydroquinone; but Zwenger (*ibid.* cxv. 108), under whose direction Uloth's experiments were made, is of opinion that the two bodies are distinct.

**ERICOLIN.** A resinous substance found in several plants of the ericaceous order, especially in the herb of the marsh wild rosemary, *Ledum palustre* (Rochleder and Schwarz, Ann. Ch. Pharm. lxxxiv. 368), less abundantly in the common heath or ling, *Calluna vulgaris* (Rochleder, *ibid.* 354), in *Rhododendron ferrugineum* (Schwarz, *ibid.* 361), and in the red bearberry, *Arctostaphylos uva ursi* (Kawaler, Wien. Acad. Ber. ix. 29).

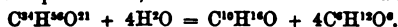
It is prepared from *Ledum palustre* by throwing the chopped leaves into boiling water and boiling for several hours; then straining the liquid; precipitating with basic acetate of lead; evaporating the filtrate in a retort to one-third of its bulk; filtering from the separated lead-salt; freeing the liquid from lead by sulphydric acid; evaporating the filtrate to an extract; and dissolving out the ericolin by anhydrous ether-alcohol. The substance left on evaporating this solvent is then repeatedly dissolved in ether-alcohol, till it no longer leaves any residue. (Rochleder and Schwarz.)

Ericolin may also be separated from the mother-liquor obtained in the preparation of arbutin from the leaves of red bearberry (i. 354), by heating that liquid with

hydrochloric or sulphuric acid; it is then deposited as a resinous precipitate, which may be purified by solution in alcohol and precipitation by water. (Kawallier.)

Ericolin obtained by the first process is a brownish-yellow powder, which cakes together at 100° C. and has a very bitter taste. Rochleder and Schwarz found it to contain (after deduction of 10·6 per cent. ash) 61·71 per cent. carbon and 7·19 hydrogen; whence they deduce the formula  $C^{24}H^{24}O^{21}$  (51·00 C and 7·00 H).

Heated with dilute sulphuric acid, it is resolved into ericicol and glucose:



**ERINITE.** A cupric arsenate, occurring in mammellated crystalline groups, of a fine emerald-green colour, in the county of Limerick, Ireland. Specific gravity = 4·043. Hardness = 4·5—5. Lustre almost dull, slightly resinous. Streak green, paler than the colour. Subtranslucent or nearly opaque. Brittle. Contains, according to an approximate analysis by Turner (Ann. Phil. [2] iv. 154), 33·78 per cent.  $As^2O^3$ , 59·44  $Cu^2O$ , 5·01 water, and 1·77 alumina; whence the formula  $5Cu^2O.As^2O^3 + 2H^2O$ , or  $Cu^5AsO^{12}.2CuHO$ .

The name *erinite* has likewise been applied to a variety of bole found at the Giant's Causeway. (See analysis *f*, i. 618.)

**ERYOPHORUM VAGINATUM.** *Hare's-tail Cotton Grass.*—The plant grown on a marshy peat soil in the neighbourhood of Berlin, yielded in the fresh state 57·13 per cent. water, 41·65 organic substance, and 1·22 ash. Of the ash, 47·43 per cent. was soluble in water, 32·03 soluble in weak nitric acid, 20·64 insoluble in nitric acid.

The ash contained in 100 pts. 32·26  $SiO^2$ , 4·59  $CO^2$ , 2·18  $SO^2$ , 6·10  $P^2O^5$ , 3·74  $Mn^2O$ , 3·86  $Fe^2O^3$ , 4·38  $Mg^2O$ , 10·48  $Ca^2O$ , 1·15  $Na^2O$ , 28·52  $K^2O$ , 2·40  $NaCl$ , 0·34  $KCl$ . (E. Witting, J. pr. Chem. lxxix. 149.)

**BRITANNIC ACID.**  $C^{14}H^{14}O^7$ .—A constituent of *Erica herbacea*. It colours iron-salts green, and is decomposed by sulphuric acid, yielding a yellow colouring matter called erixanthin.

**ERLANITE.** An imperfectly crystallised silicate from the Erzgebirg, of greenish grey colour, with traces of finely laminated structure. Specific gravity = 3·0—3·1. Hardness between apatite and felspar. Melts before the blowpipe to a clear bead, and dissolves with greenish colour in borax (Handw. d. Chem. 1<sup>re</sup> Aufl. ii. 966). According to Lampadius, it is a silicate of calcium. C. Gmelin, on the other hand, found it to contain 53·16 per cent.  $SiO^2$ , 14·03  $Al^2O^3$ , 7·14  $Fe^2O^3$ , 0·64  $Mn^2O^3$ , 14·4  $Ca^2O$ , 5·42  $Mg^2O$ , 2·61  $Na^2O$ , and 0·6 loss by ignition. (Rammelsberg's Mineralchemie, p. 771.)

**ERSEVITE.** Pure lime labradorite from Erseby in Finland, formerly regarded as anhydrous scolecite. (See LABRADORITE.)

**ERUBESCITE.** Purple copper (p. 78).

**ERUCIC ACID.**  $C^{22}H^{42}O^2$ .—An acid obtained, together with oleic acid, by the saponification of the fixed oil of white mustard (*Sinapis alba*). The oil is saponified with soda; the soap is decomposed by oleic acid; the mixture of erucic and oleic acid thus produced is treated with oxide of lead at the heat of the water-bath; the product digested with ether, which dissolves the oleate of lead; the residue treated with hydrochloric acid and alcohol; and the chloride of lead separated by filtration; the liquid is distilled to separate the alcohol; and the remaining fatty acid is boiled with water to remove hydrochloric acid, then crystallised several times from alcohol, till it exhibits a constant melting point. The fixed oil of black mustard likewise contains erucic acid.

Erucic acid crystallises in shining needles, which melt at 34° C. Its sodium-salt is soluble in alcohol. The barium-salt,  $C^{22}H^{41}BaO^2$ , is precipitated in flocks on mixing the alcoholic solutions of acetate of barium and erucate of sodium. The lead-salt,  $C^{22}H^{41}PbO^2$ , is a white precipitate obtained in like manner. The silver-salt,  $C^{22}H^{41}AgO^2$ , is a curdy precipitate, which becomes coloured on exposure to light.

**ERUCIN.** A crystalline substance, said to exist in white mustard seed. Insoluble in water, sparingly soluble in alcohol, easily in ether and in oils. Does not contain sulphur. (Simon, Pogg. Ann. xlv. 593.)

**ERYON LENS.** See LENTIL.

**ERYGLUCIN.** Syn. with ERYTHROMANNITE.

**ERYPIORIN.** Syn. with PICOERYTHRIN.

**ERYSIMUM ALLIARIA.** *Alliaria Officinalis*.—A common weed of the cruciferous order, the herb of which contains sulphocyanate of allyl (Wertheim, Ann. Ch. Pharm. lii. 52). From the seed Pless (ibid. lxxviii. 75) obtained 0·6 per cent. volatile oil containing sulphocyanate of allyl, sometimes alone, sometimes mixed with oxide of allyl.



**ERYTHRARSIN.**  $C^4H^{12}O^3As^3$ .—A red amorphous substance produced from caecodyl by combustion with insufficient access of air, by the action of hydrochloric acid and metallic tin, or of phosphorous acid, or by passing the caecodyl through slightly heated tubes. It is insoluble in water and alcohol. (See Caecodyl, i. 404.)

**ERYTHREIN.** A red substance, probably impure orcein, produced by the action of ammonia and air on erythric acid. (Heeren.)

**ERYTHRELIC ACID.** See the next article.

**ERYTHRIC ACID, or ERYTHRIN.** (Heeren, Schw. J. lix. 313. — Kane, Ann. Ch. Pharm. xxxix. 25. — Schunck, *ibid.* lxi. 69. — Stenhouse, *ibid.* lxxiii. 72; further, Proc. Roy. Soc. xii. 263. — Hesse, Ann. Ch. Pharm. cxvii. 304. — Gm. xii. 381.) — An acid discovered by Heeren in *Rocella tinctoria*; it appears also to be contained in most of the lichens from which archil is prepared. When either of these lichens — the *Rocella Montagnei*, for example — is exhausted with boiling water, the erythric acid is deposited as a crystalline powder, which may be purified by boiling alcohol. (The aqueous mother-liquor retains picroerythrin and orcein.) According to Stenhouse, it is better to exhaust the lichens with milk of lime; the quantity then obtained amounts to 12 per cent. of the weight of the lichen.

Erythric acid is white, crystalline, destitute of taste and odour, sparingly soluble in water (1 pt. of the acid requiring about 240 pts. of boiling water to dissolve it), easily soluble in alcohol, ether, and alkalis.

Erythric acid dried at  $100^\circ C$ . gives by analysis numbers agreeing nearly with either of the formulæ  $C^{20}H^{20}O^{10}$  (Stenhouse), or  $C^{20}H^{20}O^{14}$  (Hesse):

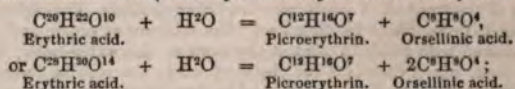
Calculation.				Hesse.		Stenhouse.		
$C^{20}$	240	56.87	$C^{20}$	336	56.95	56.9	56.84	56.94
$H^{22}$	22	5.22	$H^{20}$	30	5.08	5.4	5.56	5.33
$O^{16}$	160	37.91	$O^{14}$	224	37.97			5.63
	422	100.00		590	100.00			

Schunck found 58.70 per cent. carbon and 5.37 hydrogen, whence he deduced the formula  $C^{24}H^{19}O^{13}$ , or  $C^{24}H^{20}O^{13}$  (59.5 C, 5.5 H); Gerhardt proposed  $C^{16}H^{16}O^8$  (57.14 C, 4.77 H).

The air-dried substance was found by Hesse to contain 51.7 per cent. carbon and 5.4 hydrogen, agreeing exactly with the formula  $C^{20}H^{20}O^{14}$ ,  $2H^2O$ . When heated to  $100^\circ C$ . it gives off 5.7 per cent. water, which also agrees exactly with 2 aq. At  $137^\circ C$ . it melts, and does not solidify in the crystalline form on cooling.

*Decompositions.*—1. Erythric acid may be heated to  $200^\circ C$ . without sensible alteration; but at a higher temperature it is decomposed, yielding orcein and carbonic anhydride.

2. By boiling for some time with water, or more readily, with alkalis, it is resolved into picroerythrin and orsellinic acid (formerly called erythrelle or erythrolesic acid):



and the orsellinic acid is resolved by longer boiling into orcein ( $C^8H^6O^2$ ) and carbonic anhydride ( $CO^2$ ).

3. Boiled for some time with alcohol, it yields in like manner picroerythrin and orsellinate of ethyl,  $C^8H^7(C^2H^5)O^4$ , and with methylic alcohol orsellinate of methyl.

4. Strong sulphuric acid dissolves erythric acid without alteration in the cold; but decomposes it when heated. Boiling hydrochloric acid likewise dissolves it. Nitric acid dissolves it in the cold without evolution of nitrous acid, forming a yellow substance soluble in alcohol and precipitated by water; no oxalic acid is produced. On heating it with nitric acid, nitrous acid is evolved.

5. Bromine converts erythric acid dissolved in water into a yellow resin. When the acid is covered with ether containing water, and bromine is slowly added, tetrabromerythric acid,  $C^{20}H^{16}Br^4O^{14}$  (or  $C^{20}H^{18}Br^4O^{16}$ ), is formed, in white crystalline spherules, nearly insoluble in cold water, soluble in alcohol, slightly in cold ether. The alcoholic solution is acid, forms a white precipitate with acetate of lead, purple with a small quantity of ferric chloride, brown-red with a larger quantity; hypochlorite of sodium imparts to it a transient blood-red colour. When boiled with alcohol it is resolved into dibromorsellate of ethyl and bromopicroerythrin. Bromerythric acid cakes together a little above  $100^\circ C$ ., melts to a colourless frothy mass at  $139^\circ$ , and at a higher temperature gives off acid vapours and burns away. (Hesse.)

6. Chlorine decomposes erythric acid suspended in water, dissolving a considerable portion, and forming a yellow resinous substance. (Hesse.)

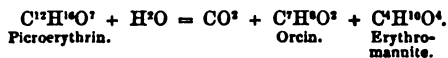
**Erythrates.**—Erythric acid is a very weak and unstable acid. It forms with *potash, soda, lime, and magnesia*, solutions which have an alkaline reaction, and from which, when recently prepared, carbonic acid throws down erythric acid; after a few days, however, no precipitate is formed. The alkaline solutions undergo decomposition when heated.

An alcoholic solution of erythric acid is not precipitated by nitrate of *silver*, but on adding ammonia a white precipitate is formed, which soon turns black and produces a specular deposit of silver. Chloride of *gold* is not altered by boiling with the alcoholic solution of erythric acid. *Sesquichloride of iron* imparts to the alcoholic solution a deep purple tint, and the addition of ammonia causes it to pass to yellow, but without precipitation, unless the liquid is boiled. The alcoholic solution of the acid is not precipitated by *neutral acetate of lead*, but with the *basic acetate* it yields a copious precipitate containing 59.12 per cent. of lead.

The compound ether obtained by boiling erythric acid with alcohol was originally regarded by Stenhouse as erythrate of ethyl,  $C^2H^{21}(C^2H^3O)^{12}$ . But as its formation is accompanied by that of picroerythrin, it appears to be orsellinate of ethyl (p. 502). It is remarkable, however, that when boiled with alkalis, it yields a solution containing both orcin and erythromannite, whereas the corresponding methylic ether treated in like manner yields orcin, but no erythromannite. The same difference is observed in the reactions of the ethylic and methylic ethers obtained from all the varieties of *Roccella tinctoria* (Stenhouse). The reaction requires further investigation.

**Picroerythrin**,  $C^2H^{14}O^7$ .—Produced by the action of boiling water on erythric acid. The acid boiled for some time with water dissolves slowly, and the liquid yields by evaporation a viscid brown mass, which, when treated with cold water, leaves picroerythrin (Schunck). Stenhouse boils erythric acid, after saturation with lime or baryta; saturates the liquid with hydrochloric acid (to precipitate erythrellic acid); filters, and leaves the solution to itself. Picroerythrin is then deposited in yellowish crystals, which may be purified by means of boiling water and animal charcoal.

Picroerythrin is colourless, crystallisable, bitter, sparingly soluble in cold water, very soluble in boiling water. The solution reddens litmus slightly. It is not altered by prolonged boiling with water, and is not etherified by alcohol. Heated in a small tube, it yields a sublimate of orcin. It dissolves in *alkalis* without the aid of heat; the ammoniacal solution quickly reddens in contact with the air. Boiled with *baryta* it yields carbonate of barium, and a solution containing orcin and erythromannite:



The aqueous solution of picroerythrin is not precipitated by *neutral acetate of lead*, but abundantly by the *basic acetate*, the precipitate containing 68.94 per cent. lead. The aqueous solution acquires a fine purple tint when mixed with *sesquichloride of iron*. It does not reduce nitrate of *silver* even at the boiling heat, unless ammonia is added. It gradually reduces chloride of *gold*.

**ERYTHRINE.** Syn. with COBALT-BLOOM (i. 1057).

**ERYTHRITE.** A flesh-coloured felspar, containing 3 per cent. magnesia, found in amygdaloid. Specific gravity = 2.541. (Thomson, Phil. Mag. [3] xxii. 188.)

**ERYTHROBETIC ACID.** A very unstable acid obtained from red beet (*Beta vulgaris*). It is crystalline, easily soluble in cold water, insoluble in alcohol and ether; precipitated from its aqueous solution by nitrate of silver and neutral acetate of lead. (Meier, Pharm. Centralbl. 1847, p. 436.)

**ERYTHRODANUM.** The name given by Kuhlmann (Ann. Ch. Phys. [2] xxiv. 225) to a red crystalline substance obtained from madder, probably impure alizarin.

**ERYTHROGEN.** A substance originally colourless, but reddened by acids, supposed by Hope (J. pr. Chem. x. 269) to be contained in flowers. Filhol regards it as identical with cyanin (p. 274).

The same name was applied by Bizio (Schw. J. xxxvii. 10) to a crystalline substance which he obtained from the bile of a patient who died of jaundice, and which he described as capable of abstracting nitrogen from the air, from nitric acid, and from ammonia, and as being converted thereby into blood-red.

**ERYTHROGENIC ACID.** An oily liquid said by Bizio to be produced on heating the substance which he calls erythrogen in oxygen gas.

**ERYTHROGLUCI-SULPHURIC ACID.** Syn. with ERYTHROMANNI-SULPHURIC ACID (p. 506).

**ERYTHROGLUCIN.** Syn. with ERYTHROMANNITE.



**ERYTHROLEIC ACID.** A purple semifluid substance said to exist in archil. (Kane, Ann. Ch. Phys. ii. 1.)

**ERYTHROLEIN** and **ERYTHROLITMIN.** Red substances obtained from litmus (q. v.)

**ERYTHROLESIC ACID.** Syn. with ERYTHRELIC ACID.

**ERYTHROLIC ACID.** The name originally applied by Kane to a substance which he supposed to exist both in archil and in litmus; subsequently, however, he applied the name *erythrolein* to the substance found in litmus, and *erythroleic acid* to the one contained in archil, because it contained more oxygen.

**ERYTHROMANNITE.**  $C^4H^{10}O^4$ . *Erythroglucin.* *Eryglucin.* *Erythrite.* *Phycite.* *Pseudorcin.* (Stenhouse, Phil. Trans. 1848, 76; 1849, 399.—Strecker, Ann. Ch. Pharm. lxxviii. 111.—Schunck, Phil. Mag. vii. 33, 254.—Lamy, Ann. Ch. Phys. [3] xxxv. 138; li. 232.—Wagner, J. pr. Chem. lxi. 125.—Hesse, Ann. Ch. Pharm. cxvii. 327.—Gm. xii. 385.) This substance exists ready formed in *Protococcus vulgaris*, and is produced by boiling erythric acid or pieroerythrin, or the ethylic ethers obtained from any of the varieties of *Rocella tinctoria* with excess of baryta or lime (p. 503). The substance from *Protococcus vulgaris* was originally called *phycite*.

*Preparation.* 1. The extract of *Lecanora Montagnei*, obtained with milk of lime, is boiled down in an open pan to about one-third or one-fourth; carbonic acid passed into the cooled liquid as long as a precipitate continues to form; and the solution, after filtration, evaporated to a syrup over the water-bath. This syrup consists chiefly of orcin and erythromannite, mixed with a rather large quantity of red colouring matter and a resinous substance. The orcin and the greater part of the colouring matter are extracted by cold ether; or the syrup is mixed with three times its volume of strong alcohol, from which, after a while, the erythromannite separates in small crystals. These are collected on a cloth filter, pressed, washed with cold strong alcohol, which dissolves the orcin and the greater part of the colouring matter, and recrystallised two or three times from hot alcohol.—2. *Protococcus vulgaris* is boiled for some hours with water, and the filtered and decolorised solution is evaporated to a syrup, precipitated with alcohol or basic acetate of lead, and the filtrate left to crystallise.—Or, 1 lb. of *Protococcus vulgaris* is digested at a temperature between  $50^\circ$  and  $100^\circ$  C. with 2 lbs. of alcohol of  $85^\circ$ ; the liquid decanted; the green residue strongly pressed out; the liquid then filtered; and the alcohol distilled to one-half. The mother-liquor of the phycic acid which is deposited on cooling, separates, when the liquid is again heated, into two layers, the alcohol at the same time evaporating. The upper layer is strongly coloured; the lower, which is less coloured, yields by evaporation a crystalline mass saturated with a black syrup, which must be pressed between fine linen, washed with very cold water, and recrystallised from hot water. (Lamy.)

*Properties.*—Large colourless transparent crystals, having an adamantine lustre, and belonging to the dimetric system. Observed faces  $P. \infty P\infty, \frac{3P3}{2}$ . Inclination of  $P : P = 123^\circ 43'$ ;  $P : \infty P\infty = 109^\circ 29'$ ;  $3P3 : \infty P\infty = 138^\circ 42'$  (Miller). Specific gravity 1.59 (Lamy). Its taste is very sweet and cooling (Lamy). Index of refraction = 1.545 (Stenhouse). Does not exhibit circular polarisation (Lamy). Melts at  $112^\circ$  C. without giving off water, and volatilises partly undecomposed (Lamy). Melts at  $120^\circ$  C. (Hesse). Does not act on litmus. Its taste is sweet, but less so than that of orcin. It does not lose water at  $100^\circ$  C. (Stenhouse). It dissolves very readily in water, sparingly in cold alcohol, and is insoluble in ether; the aqueous solution yields the finest crystals.

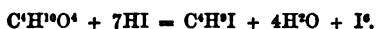
The following analyses have been made of erythromannite:—

	Calculation.		Stenhouse.	Schunck.	Lamy	
$C^4$	48	39.34	39.42	39.68	39.10	39.22
$H^{10}$	10	8.20	8.48	8.60	8.23	8.27
$O^4$	64	52.46	52.10	51.72	52.67	52.51
$C^4H^{10}O^4$	122	100.00	100.00	100.00	100.00	100.00

Stenhouse originally gave to erythromannite the formula  $C^6H^{12}O^{10}$ ; Gerhardt proposed  $C^4H^{10}O^{12}$ , or  $C^6H^{12}O^8$ , or  $C^4H^{10}O^8$ , which was first given by Strecker, and agrees best with all the reactions of erythromannite, this body may be regarded as a tetratomic alcohol,  $\left\{ \begin{smallmatrix} (C^4H^8) \\ H^4 \end{smallmatrix} \right\} O^4$ . Berthelot regards it as a hexatomic alcohol,  $C^6H^{12}O^{12} = \left\{ \begin{smallmatrix} C^2H^6 \\ H^6 \end{smallmatrix} \right\} O^{12}$ ; but this formula is improbable, on account of the uneven number of hydrogen-atoms.



**Decompositions.**—1. Erythromannite subjected to dry distillation gives off an odour of burnt sugar, and yields a liquid which does not crystallise on cooling, but dissolves in water and in alcohol (Stenhouse). It begins to boil at 160° C. without perceptible decomposition, giving off an odour of burnt flour; as the decomposition advances, the boiling point gradually rises to about 200°, but the mass does not swell up: the residue in the retort consists partly of unaltered erythromannite, partly of a substance analogous to glucose, and possessing the power of reducing copper-salts, a property not exhibited by erythromannite. Erythromannite thrown on red-hot coals gives off the odour of burnt sugar (Lamy). It burns on platinum-foil with a blue flame and an odour of caramel (Stenhouse).—2. It is not altered by aqueous potash, by ammonia, by bromine, or by chloride of lime.—3. Heated to 220° C. with solid *hydrate of potassium*, it yields acetate of potassium and hydrogen gas,  $C^4H^{10}O^4 + 2KHO = 2C^4H^5KO^2 + 2H^2O + H^2$  (Stenhouse, Lamy).—4. Fuming *nitric acid* converts it into nitro-erythromannite; on heating the mixture, oxalic acid is produced (Stenhouse).—5. Erythromannite dissolves in cold *sulphuric acid*, and when heated therewith, is converted into an erythromanni-sulphuric acid (Hesse).—6. It is not fermentable. (Stenhouse, Lamy). It does not precipitate neutral or basic acetate of lead, copper-salts, or ammonio-nitrate of lead (Stenhouse).—7. Erythromannite heated to 120° C. for a day or two, with an equal weight of tartaric acid, yields an acid having the composition  $C^4H^{10}O^4$  (Berthelot, *Compt. rend.* xlv. 268. See TARTARIC ACID).—8. Heated with *hydriodic acid* in a stream of carbonic anhydride, it yields iodide of tetrayl (V. de Luynes, *Compt. rend.* Oct. 13, 1862);



**Nitro-erythromannite.**  $C^4H(NO^2)O^4$  (Stenhouse, *Phil. Trans.* 1849, 399).—Pulverised erythromannite adding by small portions to fuming nitric acid, which is kept cool, dissolves quickly with considerable rise of temperature; and if the solution be mixed with a quantity of sulphuric acid, equal in weight to the nitric acid, or rather more, the whole forms in half an hour a crystalline magma, which is collected on a funnel plugged with asbestos, washed with cold water, pressed between paper, and recrystallised from hot alcohol. The compound is not obtained by dissolving erythromannite in a mixture of nitric and sulphuric acids, and adding water.

It forms large shining crystalline laminae, which melt at 61° C., and solidify in the crystalline form at a temperature a few degrees lower. It gives by analysis, 15.89—16.03 per cent. carbon, 2.125—2.10 hydrogen, and 18.59 nitrogen (Stenhouse, *Epistolary communication*), the above formula requiring 16.89 C, 1.99 H, and 18.54 N.

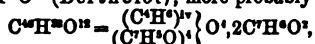
The compound takes fire when strongly heated, and burns with a bright flame. The crystals, when thoroughly dried and mixed with sand, detonate under the hammer.

**ERYTHROMANNITIC ETHERS.** *Erythroglicides. Erythrides.* (Berthelot, *Chimie organique fondée sur la Synthèse*, ii. 222.—Hesse, *loc. cit.*)—Erythromannite heated with acids to 200°—250° C. forms acid and neutral compound ethers, analogous to those derived from mannite and glycerin. These compounds are decomposed by alkalis, erythromannite being separated, and the acid sometimes uniting with the alkali, sometimes suffering further decomposition.

The *acetate* is a neutral liquid, easily soluble in alcohol and ether.

**Benzoates.**—The *dibenzoate*,  $C^{10}H^{22}O^{16}$  (Berthelot), more probably  $C^{10}H^{18}O^{16} = (C^4H^5)^2 \cdot O^4$ , is resinous when recently prepared, but gradually becomes crystalline. Insoluble in water, easily soluble in absolute alcohol and ether.

The *hexbenzoate*,  $C^{18}H^{40}O^{24}$  (Berthelot); more probably



is obtained by heating the preceding compound with ten or fifteen times its weight of benzoic acid to about 200° C. It is neutral, insoluble in water, soluble in ether.

**Orsellates.**—Berthelot regards erythrin as *diacid orsellate of erythromannite* [ $C^{10}H^{22}O^{16} = \frac{(C^4H^5)^2}{(C^4H^5O)^2} \cdot H^2 \cdot O^4$ ], and picroerythrin as the *mono-orsellate* [ $C^{11}H^{21}O^{17} = \frac{(C^4H^5)^2}{(C^4H^5O)^2} \cdot O^4$ ]. The formulæ actually given by Berthelot, viz. for erythrin  $C^{10}H^{22}O^{16} = C^2H^4O^{12} + 2C^4H^5O^4 - 6HO$ , and for picroerythrin  $C^{11}H^{21}O^{16} = C^2H^4O^{12} + C^4H^5O^4 - 4HO$ , are very improbable.

**Stearate**,  $C^{18}H^{40}O^{24}$  (Berthelot); more probably  $C^{18}H^{36}O^{24} = \frac{(C^4H^5)^6}{(C^4H^5O)^4} \cdot H^2 \cdot O^4$ . Solid, waxy, neutral body, resembling stearates in general; insoluble in water, soluble in ether.

*Sulphate, Erythromannisulphuric or Erythroglucisulphuric Acid*,  $C^8H^{11}S^2O^{14} = (C^8H^{12})^{11} \left\{ O^8 = 2C^8H^8O^4 + 3H^2SO^4 - 6H^2O \right.$ .—Produced by dissolving 1 pt. erythromannite in 20 or 30 pts. of strong sulphuric acid, and heating the solution to  $60^\circ$  or  $70^\circ$  C. It has not been prepared in the free state; but the barium or lead-salt may be obtained by diluting with water, saturating with carbonate of barium or lead, and evaporating the filtrate, first at a gentle heat, then in vacuo. The *barium-salt*,  $C^8H^{11}Ba^2S^2O^{14} + 3H^2O$ , forms a hard brittle mass, easily soluble in water, insoluble in alcohol. The *calcium-salt*,  $C^8H^{11}Ca^2S^2O^{14} + 3H^2O$ , dries up over oil of vitriol to a brittle deliquescent mass, sparingly soluble in alcohol, decomposing at  $105^\circ$  C. The *lead-salt*,  $C^8H^{11}Pb^2S^2O^{14} + 6H^2O$ , forms needle-shaped crystals, soluble in water and in alcohol. (Hesse.)

*Tartrate, Erythromannitaric Acid*.—Obtained by heating erythromannite with tartaric acid to  $100^\circ$  C. According to Berthelot, it consists of  $C^{14}H^{25}O^{50} = C^{12}H^{25}O^{12} + 4C^2H^2O^{12} - 4HO$ , and is sexbasic, its calcium-salt having the composition  $C^4H^2Ca^4O^{50}$ . Hesse suggests that it may be formed from 3 at. erythromannite; perhaps  $3C^8H^{11}O^4 + 8C^4H^2O^4 - 8H^2O = C^{14}H^{25}O^{50}$ .

**ERYTHRONIUM.** The name applied by Del Rio to a metal, which he regarded as new, contained in a peculiar lead-ore from Zimapan in Mexico. After the discovery of vanadium by Sefström, Wöhler showed that this mineral was vanadate of lead. (*Kopp's Geschichte der Chemie*, iv. 80.)

**ERYTHROPHYLL.** The red colouring matter of leaves in autumn. It is soluble in water and alcohol, and dissolves with brown colour in alkalis. With lead-salts it forms a precipitate of a fine green colour (Gerh. *Traité*, iv. 527). According to Morren (*Dissertation sur les feuilles vertes et colorées, envisagées spécialement au point de vue des rapports de la chlorophylle et de l'érythrophylle*, Gand, 1858; also N. Arch. ph. nat. v. 84), the red and blue colouring matters of plants are not formed from chlorophyll. The blue colouring matter, *anthocyan*, is probably, like litmus, the alkali-salt of an acid, which in the free state constitutes erythrophyll.

**ERYTHROPROTIDE.** A red extractive matter obtained by Mulder from albumin and allied substances. (See ALBUMIN.)

**ERYTHRORETIN.** A resinous constituent of rhubarb-root, soluble with purple-red colour in alkalis. (See RHUBARB.)

**ERYTHROSE.** The name given by Garot (J. Pharm. [3] xvii. 5) to the yellow or orange-coloured substance obtained by treating rhubarb with nitric acid, which however he allows to be a mixture. It dissolves in alkalis, forming red solutions (salts of *erythrosic acid*), which produce very deep stains. (See RHUBARB.)

**ERYTHROSIN.** Städel's name for a red substance produced by the action of nitric acid on tyrosine. (Ann. Ch. Pharm. cxvi. 87.)

**ERYTHROXYLINE.** A crystalline substance resembling theine, obtained in small quantity from the leaves of *Erythroxylon coca*. (Gaedeke, Arch. Pharm. [2] lxxxii. 141; Jahresber. d. Chem. 1855, p. 724.)

**ERYTHROXYLON COCA.** See COCA (i. 1059).

**ERYTHROZYME.** An azotised substance which exists in madder root, and gives rise to a peculiar transformation of rubian. It is extracted by macerating madder in water at  $38^\circ$  C. and precipitating the aqueous extract with alcohol. (See Madder and RUBIAN.)

**ERYTHRYLIN.** Impure erythric acid. (Kane, Ann. Ch. Pharm. xxxix. 31.)

**ESCHERITE.** A variety of epidote from the St. Gothard (probably from the Maggia Valley in Ticini), where it occurs in tuft-like masses on felspathic rocks, associated with prehnite, rock-crystal, and adularia. Specific gravity = 3.384. Gives by analysis, 37.70 to 37.62 per cent. silica, 27.49 to 27.22 alumina, 9.12 to 8.67 ferric oxide, 23.87 to 23.94 lime, and 2.33 water. (Stockar-Escher, Pogg. Ann. xcv. 501.)

**ESCHHOLTZIA CALIFORNICA.** This papaveraceous plant contains, according to Walz (Jahrb. pr. Pharm. vii. 282; viii. 147, 209), colouring matters, citric and malic acids, a peculiar acid, and three alkaloids, viz. 1. An alkaloid forming red salts, and perhaps identical with chelerythrine (i. 847).—2. An alkaloid soluble in alcohol and ether, and forming bitter sharp-tasting salts; its properties are essentially those of chelidonine (i. 849). These two alkaloids are extracted from the plant by acidulated water, and precipitated by ammonia.—3. An alkaloid precipitated from the mother-liquor of the other two by tannic acid. It is crystalline, has a nauseous taste,

dissolves in water, alcohol, and ether; melts at a gentle heat, and forms salts, which, even in dilute solution, assume a splendid violet colour on addition of sulphuric acid.

All these bodies require further investigation.

**ESCHWEGITE.** A mineral examined by Döbereiner (*Glocker's Synopsis*, p. 86), and said to contain ferrous oxide and silica.

**ESCOLIN.** See *ÆSCULIN*.

**ESSENBECKINE.** An alkaloid obtained from the bark of *Esenbeckia febrifuga*, Mart. *Evodia febrifuga*, Aug. Saint Hilaire. (Buchner, *Repert. Pharm.* xxxi. 481; xxxvii. 1.)

**ESMARKITE.** A variety of hydrous dichroite from Brevig in Finland. The term is also used as a synonyme of datholite, and appears also to have been applied to an altered form of scapolite. (Dana, ii. 205.)

**ESPARSETTE.** See *HEDYSARUM*.

**ESRAE.** A narcotic substance resembling tobacco, extracted from the leaves of *Atropa Mandragora*. (Landerer, *Buchn. Repert.* lxxxi. 290.)

**ESSENCES.** A term sometimes applied to volatile oils.

**ESSONITE.** A variety of lime-garnet.

**ESTER.** L. Gmelin's name for compound ethers derived from oxygen acids, e.g. acetate of ethyl = *Essigsäure-ester*; sulphate of methyl = *Schwefelsaures Formester*.

**ETHAL.** Syn. with *CETYLIC ALCOHOL* (i. 841).

**ETHALIC ACID.** Syn. with *PALMITIC ACID*.

**ETHALOL.** The name applied by Berzelius to the hydrocarbon (cetene) produced by the action of phosphoric anhydride on cetyl alcohol.

**ETHALONE** or *Cetylone*. Syn. with *PALMITONE*.

**ETHALYL.** Syn. with *CETYL*.

**ETHAMIDE, ETHAMINE, ETHAMMINE.** Syn. with *ETHYLAMINE*.

**ETHAMINE-SULPHURIC ACID.** Syn. with *SULPHETHAMIC ACID*.

**ETHENE.** Syn. with *ETHYLENE*.

**ETHENIDES.** Laurent's name for *Primary Nuclei*. (See *NUCLEUS*.)

**ETHER.** See *ETHYL OXIDE* &c.; also *ETHERS*.

**ETHERENE.** Syn. with *ETHYLENE*.

**ETHERIFICATION.** The conversion of alcohols into ethers. (See *ALCOHOL*, i. 76; *ALCOHOLS*, i. 99; *CHEMICAL AFFINITY*, i. 867; *ETHERS*, ii. 608.)

**ETHERIN** and **ETHEROL.** (Marchand, *J. pr. Chem.* xv. 1.—Serullas, *Ann. Ch. Phys.* [2] xxxix. 162; *Pogg. Ann.* xiv. 20.—Liebig, *Handw. d. Chem.* 1<sup>te</sup> Aufl. i. 121.) When heavy oil of wine, the oily body which sometimes occurs among the residues of the preparation of ether, is warmed with water, a light oily liquid rises to the surface, which is a mixture of two substances, both polymeric with ethylene, viz. etherin and etherol. On decanting this liquid and leaving it at rest, the etherin crystallises out, while the etherol remains liquid. The etherin may be freed from etherol by filtration and pressure between paper, and then recrystallised from alcohol or ether.

*Etherin* forms transparent, colourless, shining prisms, moderately hard, very friable and grating between the teeth; it has no taste, but when heated smells like etherol. Melts at 110° C. Boils at 260°, without alteration. Insoluble in water, but soluble in alcohol, and still more so in ether.

*Etherol* is a yellowish, viscid liquid of specific gravity 0.921 (Serullas), boiling at 280° C. By exposure to cold, it becomes more viscid, but does not solidify even at -36° C. It has a peculiar aromatic odour, is insoluble in water, but dissolves easily in ether, less easily in alcohol. Potassium immersed in it retains its lustre undiminished.

*Heavy oil of wine*, which passes over in the preparation of ether towards the end of the distillation, when sulphurous anhydride and olefiant gas are given off, is, according to Liebig, an ethylsulphate of etherol. On treating it with water, the etherol (holding the isomeric body etherin in solution) separates out, and ethylsulphuric acid remains in solution. An oil of similar character and composition is obtained by the distillation of perfectly dry ethylsulphates, the best process, according to Liebig, being to distil the dry potassium-salt with an equal weight of freshly burned lime. Mar-



chand recommends the distillation of dry ethylsulphate of lead. The crude product is freed from alcohol, ether, and sulphurous acid, by agitation with cold water, and drying in vacuo over oil of vitriol.

*Light oil of wine*, which is also obtained in the preparation of ether on the large scale appears to be impure etherol. When the crude ether is rectified with milk of lime, this substance remains after the ether has passed over, floating on the watery residue, in the form of a thick yellow oil, which is blackened by strong sulphuric acid, but separates as a colourless oil on addition of water.

**ETHERINAMONE.** Syn. with ETHYLAMINE.

**ETHERIPLATINIC ACID.** Syn. with ETHYLENE-CHLORIDE OF PLATINUM.

**ETHEROL.** See ETHERIN.

**ETHERONE.** A very volatile liquid, boiling at about  $30^{\circ}\text{C}$ ., which passes over with the heavy oil of wine produced by the distillation of the ethyl-sulphates (Marchand J. pr. Chem. xv. 1). It appears to be identical with amylene.

**ETHERS.** The term *ether*, originally applied to oxide of ethyl, the volatile liquid produced by the action of sulphuric acid upon common alcohol, is now extended to a large class of compounds, formed by the action of acids on alcohols, and includes all salts of alcohol-radicles, that is to say, all such derivatives of the alcohols as are comparable with ordinary metallic salts, in the same sense as the alcohols themselves are comparable with metallic hydrates.

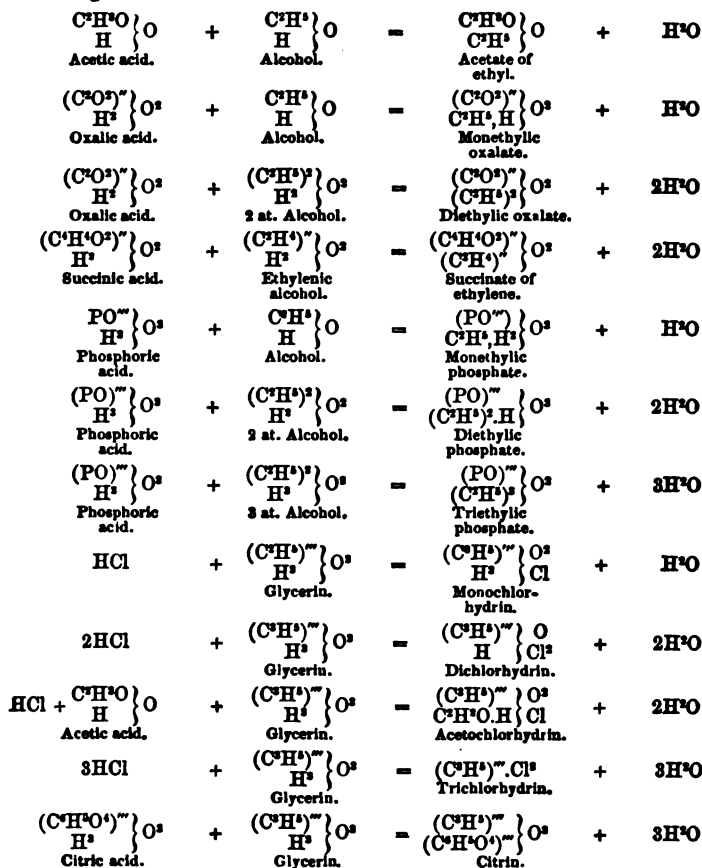
Some of these bodies, commonly called simple ethers (Gmelin's *Aether*), are the oxides of the alcohol-radicles, and may be regarded as the anhydrides of the alcohols, being related to them in the same manner as an anhydrous metallic oxide to its hydrate. With these may also be classed the sulphides, selenides, and tellurides of the alcohol-radicles. The remaining ethers, called compound ethers, which constitute by far the most numerous class, are analogous to metallic salts, and are usually subdivided into two groups, the one comprising the oxygen-salts of the alcohol-radicles (Gmelin's *Ester*), the other, the haloïd salts of those radicles, viz. the chlorides, bromides, iodides, fluorides, and cyanides (Gmelin's *Afer*). The former may be derived from a single or multiple molecule of water, in which part of the hydrogen is replaced by acid-radicles, and the remainder (not necessarily the whole) by alcohol-radicles, e.g.

Types. $\begin{matrix} \text{H} \\ \text{H} \end{matrix} \left\{ \begin{matrix} \text{O} \\ \text{O} \end{matrix} \right\}$	$\begin{matrix} \text{C}^2\text{H}^3 \\ \text{C}^2\text{H}^3\text{O} \end{matrix} \left\{ \begin{matrix} \text{O} \\ \text{O} \end{matrix} \right\}$			
	Acetate of ethyl.			
$\begin{matrix} \text{H}^2 \\ \text{H}^2 \end{matrix} \left\{ \begin{matrix} \text{O}^2 \\ \text{O}^2 \end{matrix} \right\}$	$\begin{matrix} \text{C}^2\text{H}^3.\text{H} \\ (\text{SO}^2)'' \end{matrix} \left\{ \begin{matrix} \text{O}^2 \\ \text{O}^2 \end{matrix} \right\}$	$\begin{matrix} (\text{C}^2\text{H}^3)^2 \\ (\text{SO}^2)'' \end{matrix} \left\{ \begin{matrix} \text{O}^2 \\ \text{O}^2 \end{matrix} \right\}$		
	Monethylic sulphate.	Diethylic sulphate.		
$\begin{matrix} \text{H}^3 \\ \text{H}^3 \end{matrix} \left\{ \begin{matrix} \text{O}^3 \\ \text{O}^3 \end{matrix} \right\}$	$\begin{matrix} \text{C}^2\text{H}^3.\text{H}^2 \\ (\text{PO})''' \end{matrix} \left\{ \begin{matrix} \text{O}^3 \\ \text{O}^3 \end{matrix} \right\}$	$\begin{matrix} (\text{C}^2\text{H}^3)^2.\text{H} \\ (\text{PO})''' \end{matrix} \left\{ \begin{matrix} \text{O}^3 \\ \text{O}^3 \end{matrix} \right\}$	$\begin{matrix} (\text{C}^2\text{H}^3)^3 \\ (\text{PO})''' \end{matrix} \left\{ \begin{matrix} \text{O}^3 \\ \text{O}^3 \end{matrix} \right\}$	
	Monethylic phosphate.	Diethylic phosphate.	Triethylic phosphate.	

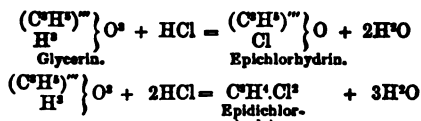
The haloïd-compounds of the alcohol-radicles may be regarded as formed on the hydrogen-type  $\text{nHH}$ , the hydrogen being partly replaced by an alcohol-radicle, partly by chlorine, bromine, &c., e.g. *chloride of ethyl*,  $\text{C}^2\text{H}^3\text{Cl}$ , *dibromide of ethylene* ( $\text{C}^2\text{H}^4$ ) $\text{Br}^2$ , *tribromide of glyceryl* ( $\text{C}^3\text{H}^5$ ) $\text{Br}^3$ ; or they may be derived from water regarded as  $\text{H.HO}$ , by supposing the  $\text{HO}$  replaced by an equivalent quantity of chlorine, &c., and the hydrogen by an alcohol-radicle. This mode of derivation may also evidently be extended to the oxygen-salts of the alcohol-radicles, the  $\text{HO}$  in the type being supposed to be replaced by the peroxide of an acid-radicle; in fact, it really amounts to regarding all the so-called compound ethers as formed upon the hydrogen or hydrochloric acid type: thus, *acetate of ethyl*,  $\text{C}^2\text{H}^3.\text{C}^2\text{H}^3\text{O}^2$ ; *monethylic sulphate*,  $\text{C}^2\text{H}^3.\text{SO}^2$ ; *diethylic phosphate*,  $\begin{matrix} (\text{C}^2\text{H}^3)^2 \\ \text{H} \end{matrix} \left\{ \begin{matrix} \text{O}^3 \\ \text{O}^3 \end{matrix} \right\} \text{PO}^4$ , &c. It is convenient in this respect—that it reduces all these compounds to the same type, which likewise includes a number of intermediate compounds, such as the chlorhydrins, chloracetins, &c.

Type. $\begin{matrix} \text{H}^2 \\ \text{H}^2 \end{matrix} \left\{ \begin{matrix} \text{HO} \\ \text{HO} \end{matrix} \right\}$	$\begin{matrix} (\text{C}^2\text{H}^3)'' \\ \text{Cl} \end{matrix} \left\{ \begin{matrix} \text{HO} \\ \text{Cl} \end{matrix} \right\}$	$\begin{matrix} (\text{C}^2\text{H}^3)'' \\ \text{Cl} \end{matrix} \left\{ \begin{matrix} \text{C}^2\text{H}^3\text{O}^2 \\ \text{Cl} \end{matrix} \right\}$	$\begin{matrix} (\text{C}^2\text{H}^3)'' \\ \text{Cl} \end{matrix} \left\{ \begin{matrix} \text{Cl} \\ \text{Cl} \end{matrix} \right\}$
	Glycolic Chlorhydrin.	Glycolic Chloracetin.	Dichloride of ethylene.
$\begin{matrix} \text{H}^3 \\ \text{H}^3 \\ \text{H}^3 \end{matrix} \left\{ \begin{matrix} \text{HO} \\ \text{HO} \\ \text{HO} \end{matrix} \right\}$	$\begin{matrix} (\text{C}^2\text{H}^3)''' \\ \text{Cl} \end{matrix} \left\{ \begin{matrix} \text{HO} \\ \text{HO} \\ \text{Cl} \end{matrix} \right\}$	$\begin{matrix} (\text{C}^2\text{H}^3)'' \\ \text{Cl} \end{matrix} \left\{ \begin{matrix} \text{HO} \\ \text{Cl} \\ \text{Cl} \end{matrix} \right\}$	$\begin{matrix} (\text{C}^2\text{H}^3)''' \\ \text{Cl} \end{matrix} \left\{ \begin{matrix} \text{Cl} \\ \text{Cl} \\ \text{Cl} \end{matrix} \right\}$
	Chlorhydrin.	Dichlorhydrin.	Trichlorhydrin.

The compound ethers contain the elements of an acid and an alcohol, *minus* a certain number of molecules of water. If the quantities of acid and alcohol concerned in the reaction are of equal atomicity, *i. e.* contain the same number of atoms of replaceable hydrogen, then the number of molecules of water eliminated in the formation of the ether corresponds for the most part to that number of hydrogen-atoms; but if the atomicities of the acid and alcohol are unequal, the number of molecules of water eliminated corresponds to the smaller atomicity of the two. With the monatomic alcohols, this rule is universally true, but the polyatomic alcohols present an exception to it, to be presently noticed. The following examples will suffice to illustrate the general rule:—



In all these cases, the resulting ether is of the same degree of atomicity as the higher of the two bodies concerned in its formation; but the polyatomic alcohols are capable of forming ethers, with elimination of a number of molecules of water greater than that indicated by the preceding rule, thereby yielding compounds of a lower type; thus:—



See also the BROMHYDRINS (*i.* 668), and GLYCIDE.

When the process of etherification is so conducted that the compound ether and the water produced remain in contact, they react upon each other, tending to reproduce the

original acid and alcohol. Unless, therefore, the water is removed as fast as it is formed, the quantity of the compound ether produced is always less than that which the given quantities of acid and alcohol are capable of yielding. The manner in which the quantity of ether ultimately formed, and the rapidity of the action, are affected by the nature of the acid and alcohol, their relative quantities, the temperature, and other conditions of the reaction, has been examined by Berthelot and Péan de Saint-Gilles (Compt. rend. liii. 474; lv. 39, 210 and 324; Rép. Chim. pure 1862, pp. 1, 325, 327, 369), who have obtained the following results:—

1. The quantities of acid and alcohol which *ultimately* enter into combination are independent of the temperature and pressure at which the reaction takes place, and are but little affected by the particular nature of the acid and alcohol concerned, the variations observed appearing to depend on accidental causes.

2. The *rapidity of combination*, or, in other words, the quantity of the compound ether formed in a given time, varies with the nature of the acid and the alcohol, and with the proportions in which they are mixed.

a. The rapidity of combination of an acid of the series  $C^mH^nO^2$  with an alcohol, is less in proportion as the atomic weight of the acid is greater, and its boiling point higher.

The same law applies to monobasic acids of different series; thus, acetic acid etherifies alcohol more quickly than benzoic acid.

Polybasic acids etherify alcohols more quickly than monobasic acids.

b. Alcohols of the same series,  $C^mH^{2m+2}O$ , for example, are etherified by any given acid with nearly equal rapidity, how much soever their molecular weights may differ. This is not true, however, with regard to alcohols of different series; thus, glycerin unites with acetic acid at common temperatures much more readily than common alcohol.

c. With a given quantity of acid, the quantity of ether ultimately produced increases with the quantity of alcohol present; but the rapidity of combination is diminished by an excess of alcohol at the beginning of the action, and increased thereby as it approaches the limit.

d. With a given quantity of alcohol, the quantity of ether ultimately formed increases with the proportion of acid present. At ordinary temperatures, the rapidity of combination is for the most part diminished by excess of acid at first and accelerated afterwards. With 5 at. of a monobasic acid to 5 at. of a monatomic alcohol, the rate of combination is accelerated, even from the beginning. At  $100^\circ C$ . the accelerating influence of an excess of acid is still more marked.

3. The ethers of monobasic acids resist the action of water longer than those of polybasic acids. The amount of resistance which a compound ether offers to the decomposing action of water is determined by the nature of the acid, not of the alcohol, concerned in its formation. In general, the ethers corresponding to acids which are most difficult to etherify, are likewise those which offer the greatest resistance to the action of water; thus butyrate of ethyl is less easily decomposed than the acetate, and this less easily than the formate.

The quantity of an ether decomposed by water increases with the quantity of water present; but ethers are never completely decomposed, even by a very great excess of water; neither can such an excess completely prevent the combination of an alcohol and an acid, though it diminishes the total quantity of ether produced.

4. Pressure appears to influence the phenomena of etherification, as well as of other kinds of chemical action, not directly, but only so far as it affects the proximity of the molecules of the acting substances. Hence when both bodies are in the liquid state, which admits of but little variation in the molecular intervals, the result is but slightly affected even by great variations of pressure; but when the acting bodies are wholly or partly in the gaseous state, as when acetic acid and alcohol are heated together in closed vessels to  $200^\circ C$ ., the action is retarded by diminution of pressure. On the other hand, the authors' experiments have brought out the somewhat unexpected result that the limit of the quantity of ether producible from a given quantity of an acid and alcohol, becomes greater as the intermolecular distance is increased.

We proceed to enumerate some of the principal ethers, and give a general view of their formation and reactions.

#### Ethers containing Monatomic Alcohol-radicles.

##### 1. Oxides.

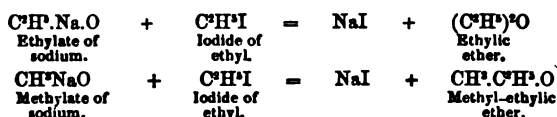
Methylic oxide . . .	$\left. \begin{array}{c} CH^3 \\ CH^3 \end{array} \right\} O$	Ethylic oxide . . .	$\left. \begin{array}{c} C^2H^3 \\ C^2H^3 \end{array} \right\} O$
Methyl-ethylic oxide . . .	$\left. \begin{array}{c} CH^3 \\ C^2H^3 \end{array} \right\} O$	Ethyl-tetrylic oxide . . .	$\left. \begin{array}{c} C^2H^3 \\ C^4H^3 \end{array} \right\} O$



Tetrylic oxide . . . . .	$\left. \begin{matrix} \text{C}^4\text{H}^8 \\ \text{C}^4\text{H}^8 \end{matrix} \right\} \text{O}$	Octylic oxide . . . . .	$\left. \begin{matrix} \text{C}^8\text{H}^{16} \\ \text{C}^8\text{H}^{16} \end{matrix} \right\} \text{O}$
Methyl-amylic oxide . . . . .	$\left. \begin{matrix} \text{C}^3\text{H}^6 \\ \text{C}^3\text{H}^{11} \end{matrix} \right\} \text{O}$	Ethyl-cetylic oxide . . . . .	$\left. \begin{matrix} \text{C}^2\text{H}^4 \\ \text{C}^{16}\text{H}^{32} \end{matrix} \right\} \text{O}$
Ethyl-amylic oxide . . . . .	$\left. \begin{matrix} \text{C}^2\text{H}^4 \\ \text{C}^3\text{H}^{11} \end{matrix} \right\} \text{O}$	Cetylic oxide . . . . .	$\left. \begin{matrix} \text{C}^{16}\text{H}^{32} \\ \text{C}^{16}\text{H}^{32} \end{matrix} \right\} \text{O}$
Amylic oxide . . . . .	$\left. \begin{matrix} \text{C}^3\text{H}^6 \\ \text{C}^3\text{H}^{11} \end{matrix} \right\} \text{O}$	Allylic oxide . . . . .	$\left. \begin{matrix} \text{C}^3\text{H}^6 \\ \text{C}^3\text{H}^6 \end{matrix} \right\} \text{O}$
Methyl-octylic oxide . . . . .	$\left. \begin{matrix} \text{C}^3\text{H}^6 \\ \text{C}^8\text{H}^{17} \end{matrix} \right\} \text{O}$	Ethyl-allylic oxide . . . . .	$\left. \begin{matrix} \text{C}^2\text{H}^4 \\ \text{C}^3\text{H}^6 \end{matrix} \right\} \text{O}$
Ethyl-octylic oxide . . . . .	$\left. \begin{matrix} \text{C}^2\text{H}^4 \\ \text{C}^8\text{H}^{17} \end{matrix} \right\} \text{O}$	Phenylic oxide . . . . .	$\left. \begin{matrix} \text{C}^6\text{H}^8 \\ \text{C}^6\text{H}^8 \end{matrix} \right\} \text{O}$
Amyl-octylic oxide . . . . .	$\left. \begin{matrix} \text{C}^5\text{H}^{10} \\ \text{C}^8\text{H}^{17} \end{matrix} \right\} \text{O}$	Benzylic oxide . . . . .	$\left. \begin{matrix} \text{C}^7\text{H}^8 \\ \text{C}^7\text{H}^8 \end{matrix} \right\} \text{O}$

The compounds obtained by the action of potassium or sodium on the alcohols, such as *ethylo-sodic oxide*, *ethylate of sodium*, or *sodium-alcohol*,  $\text{C}^2\text{H}^4\text{NaO}$ , are bodies of analogous constitution; but as the metal is easily replaceable by an alcohol-radicle, they are perhaps more like alcohols than ethers. The oxides of some of the organo-metallic bodies, such as oxide of cacodyl ( $\text{C}^2\text{H}^4\text{As}$ ) $_2\text{O}$ , are also analogous in composition to those in the preceding lists, but they are not usually classed as ethers.

The simple ethers are produced: 1. By the action of the iodides, bromides, or chlorides of the alcohol-radicles on the potassium- or sodium-alcohols, *e. g.*:



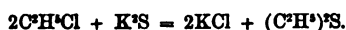
2. By distilling an alcohol or a mixture of two alcohols with sulphuric acid (i. 76, 78).

Oxide of methyl is gaseous; oxide of cetyl and ethyl-cetylic oxide are solid and crystalline; all the other ethers in the preceding list are liquids, more or less mobile, and capable of volatilising without decomposition. They are all neutral to vegetable colours. With *acids* they behave, for the most part, like the alcohols; thus oxide of ethyl treated with sulphuric acid, yields acid sulphate of ethyl, and with hydrochloric acid, chloride of ethyl. *Persulphide of phosphorus* transforms them into sulphides. Altogether, however, they are less energetic in their chemical relations than the alcohols, just as anhydrous metallic oxides act, for the most part, less energetically than the corresponding hydrates.

The simple ethers, treated with *chlorine*, yield chlorinated ethers, such as  $(\text{CH}^1\text{Cl})_2\text{O}$ ,  $(\text{C}^2\text{H}^4\text{Cl})_2\text{O}$ , &c. By treating dichlorethylic ether  $(\text{C}^2\text{H}^4\text{Cl})_2\text{O}$  with *zinc-ethyl*, an atom of chlorine is removed, and its place supplied by ethyl, forming the compound  $\left. \begin{matrix} \text{C}^2\text{H}^4(\text{C}^2\text{H}^5) \\ \text{C}^2\text{H}^4\text{Cl} \end{matrix} \right\} \text{O}$ ; and this product again treated with zinc-ethyl, yields the compound  $\left. \begin{matrix} \text{C}^2\text{H}^4(\text{C}^2\text{H}^5) \\ \text{C}^2\text{H}^4(\text{C}^2\text{H}^5) \end{matrix} \right\} \text{O}$ . (Lieben and Bauer, Ann. Ch. Pharm. cxxiii. 130.)

## 2. Sulphides, Selenides, and Tellurides of Monatomic Alcohol-radicles.

The protosulphides of the monatomic alcohol-radicles, called *sulphydric ethers*, are exactly analogous in composition to the oxides, *e. g.* *sulphide of ethyl* =  $\left. \begin{matrix} \text{C}^2\text{H}^5 \\ \text{C}^2\text{H}^5 \end{matrix} \right\} \text{S}$ . They are produced by the action of the chlorides, iodides, or sulphates of the corresponding alcohol-radicles on the protosulphides of the alkali-metals, *e. g.*:



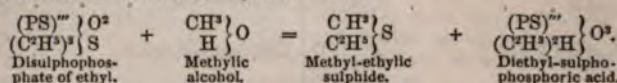
Also by the action of pentasulphide of phosphorus on the corresponding oxygenethers:



By these means, the sulphides of *methyl*, *ethyl*, *amyl*, *octyl*, *cetyl*, and *allyl* have been obtained; the last-mentioned sulphide is also the essential constituent of volatile oil of garlic (i. 143).

These compounds, which are the ethers of the sulphydric alcohols, or mercaptans, are fetid oils or crystalline solids, insoluble in water. Treated with *nitric acid*, they yield monobasic acids containing sulphur and oxygen: sulphide of ethyl, for example, yields ethyl-sulphurous acid,  $\text{C}^2\text{H}^5\text{H}(\text{SO})^{\text{H}}\text{O}^2$ . With *chlorine*, they yield substitution-products.

*Sulphides containing two alcohol-radicles*, analogous to methyl-ethylic oxide, &c., are obtained by heating in a sealed tube a mixture of an alcohol with the disulphophosphate of another alcohol-radicle, thus:

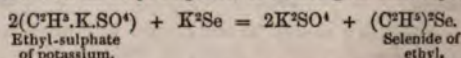


*Ethyl-amylic sulphide*,  $\text{C}^2\text{H}^5\text{C}^3\text{H}^7\text{S}$ , is obtained in a similar manner. These compounds are volatile liquids, resembling the simple alcoholic sulphides in their physical and chemical properties. (Carius, Ann. Ch. Pharm. cxix. 313.)

The mercaptans treated with metals or metallic oxides, yield sulphides containing a metal and an alcohol-radicle; thus ethylic mercaptan treated with sodium yields *ethylo-sodic sulphide*,  $\text{C}^2\text{H}^5\text{NaS}$ . Such compounds treated with the iodide of another alcohol-radicle, appear to yield mixed alcoholic sulphides, like those above mentioned. See Ann. Ch. Pharm. cxx. 62.

Persulphides of alcohol-radicles, such as  $\text{CH}^3\text{S}$ ,  $\text{C}^2\text{H}^5\text{S}$ , analogous to peroxide of hydrogen, are obtained by the action of the chlorides or acid sulphates of those radicles on the persulphides of the alkali-metals. They are related to the protosulphides above mentioned in the same manner as peroxide of hydrogen to water. They are fetid liquids, heavier than water, and volatile without decomposition. With nitric acid, they yield the same products as the protosulphides. Their alcoholic solutions yield white precipitates with acetate of lead and mercuric chloride.

The selenides and tellurides of the alcohol-radicles, *e.g.*  $(\text{C}^2\text{H}^5)^2\text{Se}$  and  $(\text{C}^2\text{H}^5)^2\text{Te}$ , are obtained like the corresponding sulphides, viz. by distilling a metallic selenide or telluride with an ethyl-sulphate, or homologous salt, *e.g.*:



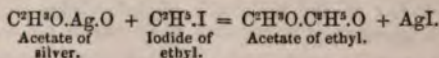
The *methyl*-, *ethyl*-, and *amyl*-compounds of *selenium* and *tellurium* have been obtained. They are extremely fetid oily liquids, heavier than water. By exposure to the air, they are converted into basic oxides, *e.g.*  $(\text{C}^2\text{H}^5)^2\text{SeO}$ , capable of forming salts with acids. They are likewise oxidised by nitric acid and converted into nitrates. This basic property of the alcoholic selenides and tellurides, which is possessed in a slight degree only by the corresponding sulphides, approximates them to the organo-metallic bodies, the arsenethylys, stannethylys, &c.

### 3. Oxygen-salts of Monatomic Alcohol-radicles.

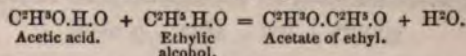
#### a. Containing Monatomic Acid-radicles.

These ethers may be derived from monobasic acids by the substitution of an alcohol-radicle for the basic hydrogen. They are very numerous; in fact, every monobasic acid appears to be capable of forming such compounds, at least with the alcohol-radicles containing but a small number of carbon-atoms, such as methyl and ethyl. They are produced:

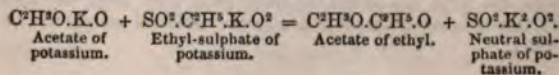
1. By the action of a silver-salt on the iodide, bromide, or chloride of an alcohol-radicle:



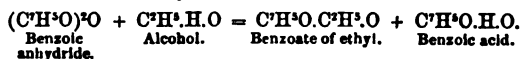
2. By the reaction of an acid with an alcohol, especially with aid of heat:



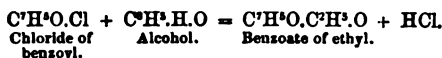
3. By distilling a metallic salt with sulphuric acid and an alcohol, or by passing hydrochloric acid gas into an alcoholic solution of an acid.—4. By the dry distillation of a metallic salt of an acid ether (*e.g.* ethyl-sulphate of potassium) with the salt of another acid:



6. By the solution of an acid anhydride in an alcohol:

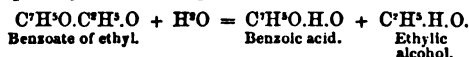


6. By the action of an acid chloride on an alcohol:



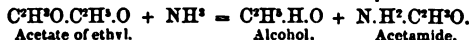
The stronger mineral acids, such as sulphuric and nitric acid, etherify the alcohols directly; oxalic acid etherifies ethylic alcohol when the latter is added drop by drop to the acid at a high temperature. Sometimes the etherification takes place gradually when the acid and the alcohol are mixed together, and exposed for some days to a gentle heat; such, according to Liebig, is the case with oxalic acid. Generally speaking, however, organic acids etherify the alcohols only when assisted by sulphuric or hydrochloric acid, or when heated for a long time with the alcohol in sealed tubes. The mineral acid probably acts by abstracting the water set free in the etherification; or its influence may be similar to that which, according to Berthelot and Péan de Saint-Gilles (p. 510), is produced by an excess of the etherifying acid. The alcohols are etherified by anhydrides much more quickly than by acids, and still more easily by the chlorides of the acid radicles. Some organic acids (benzoic, butyric, palmitic) produce compound ethers when heated with the simple ethers (oxides) to 360° or 400° C. in a sealed tube. (Berthelot.)

The monatomic oxygen-ethers are liquid or solid bodies volatile without decomposition. The boiling point of a monatomic methyl-ether is about 63° C. below that of the corresponding acid, that of an ethyl-ether about 44° C. below that of the acid. They are insoluble or sparingly soluble in water, but mix in all proportions with common alcohol and ether. They do not immediately exhibit the reactions of the acids from which they are derived; but by prolonged contact with water, they are resolved more or less quickly, especially at the boiling heat, into acid and alcohol, *e.g.*:

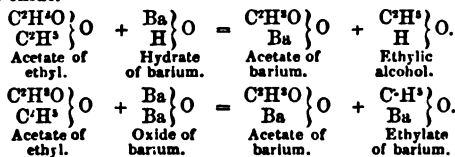


This transformation is more quickly effected by boiling with *caustic alkalis*, especially in alcoholic solution; it is likewise produced by the stronger *acids*, such as sulphuric or hydrochloric acid. The ethers may be distinguished one from the other by the properties of the acid and alcohol thus obtained from them.

The monatomic compound ethers are converted by *ammonia* into an alcohol and an amide, *e.g.*:



The ethers are likewise decomposed by the more basic *anhydrous oxides*, when heated therewith in sealed tubes, the action being similar to that which takes place with the alkaline hydrates, excepting that, instead of an alcohol, a metallic alcoholate is formed in the first instance, and this, when treated with water, yields the alcohol and a metallic hydrate. The following equations exhibit the reactions with a hydrated and an anhydrous oxide.



(Berthelot and Fleurieu, Compt. rend. li. 1020).

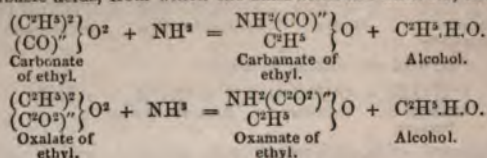
The cyanates of the alcohol-radicles form a group of monatomic ethers, which are distinguished by particular reactions, inasmuch as, under the influence of water and alkalis, they split up as if they were formed on the ammonia-type instead of the water-type; thus cyanate of ethyl may be represented either as  $\text{C}^6\text{H}_5 \} \text{O}$  or as

$\text{N} \{ \text{C}^6\text{H}_5 \} \text{CO}$ . Accordingly, when treated with water, they yield compound ureas; also when treated with ammonia, ethylamine, phenylamine, and other organic bases. When distilled with caustic alkalis, they yield an alkaline carbonate and an amine. (See CYANIC ETHERS, p. 195.)

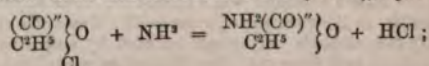
Another class of monatomic ethers requiring special notice are the *a methanes*, or



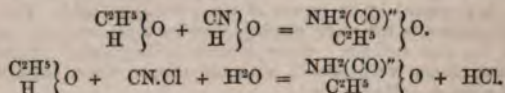
ethers of amic acids. They are obtained by the action of ammonia on the neutral ethers of the dibasic acids, from which the amic acids are derived; thus



The *alcoholic carbamates*, or *carbamethanes*, or *urethanes*, may also be obtained by the action of ammonia on the chlorocarbonic ethers (i. 916), *e. g.* :

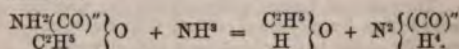


or by the action of cyanic acid vapour, or gaseous chloride of cyanogen, on the alcohols:

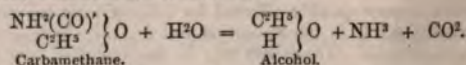


The oxamates of methyl, ethyl, and amyl have been obtained; also the carbamates of the same radicles, together with carbamate of tetryl.

The amethanes are solid, crystallisable bodies, which are converted by ammonia into an alcohol and a diamide:



They are decomposed by alkalis, by boiling mineral acids, and partially by water, the carbamethanes yielding an alcohol, ammonia, and carbonic anhydride, the oxamethanes the same products, with addition of carbonic oxide:



The acids formed from carbamic acid by the substitution of an alcohol-radicle for part of the hydrogen in the ammonium-molecule may also be mentioned here: *e.g.* ethyl-carbamic acid,  $\left\{ \begin{array}{l} \text{NH}(\text{C}^2\text{H}^5)(\text{CO})'' \\ \text{H} \end{array} \right\} \text{O}$  (i. 751).

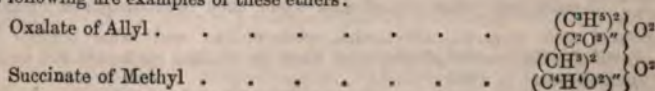
A few monatomic compound ethers are known, in which the oxygen is wholly or partly replaced by sulphur, *viz.* *thiacetate of ethyl*,  $\left\{ \begin{array}{l} \text{C}^2\text{H}^5 \\ \text{C}^2\text{H}^5\text{O} \end{array} \right\} \text{S}$ , and the *sulphocyanic ethers*, such as *sulphocyanate of ethyl*,  $\left\{ \begin{array}{l} \text{C}^2\text{H}^5 \\ \text{Cy} \end{array} \right\} \text{S}$ , and *sulphocyanate of allyl*,  $\left\{ \begin{array}{l} \text{C}^3\text{H}^5 \\ \text{Cy} \end{array} \right\} \text{S}$ , which is the principal constituent of volatile oil of mustard.

#### b. Containing Diatomic Acid-radicles.

These ethers may be derived from dibasic acids by the partial or total replacement of the typic hydrogen by a monatomic alcohol-radicle. The ether is acid or neutral, according as half or the whole of the typic hydrogen is thus replaced.

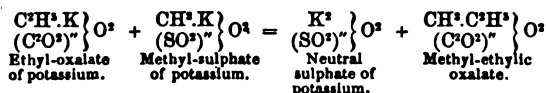
The neutral diatomic ethers of monatomic alcohol-radicles are produced by the same reactions as the monatomic compound-ethers (p. 512). When the corresponding acids are not volatile without decomposition, these ethers (those of malic and tartaric acids, for example) are decomposed by distillation, and cannot therefore be prepared by that process. They are usually obtained by passing hydrochloric acid gas into a solution of the organic acid in the alcohol, neutralising the resulting liquid with carbonate of sodium, then shaking it up with common ether, which dissolves the compound ether produced, and evaporating the solvent.

The following are examples of these ethers:

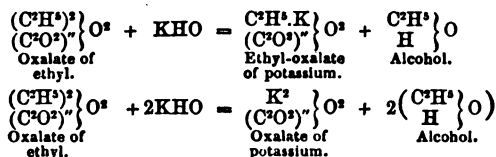




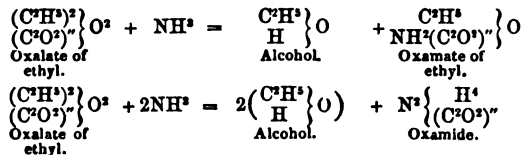
There are also diatomic ethers containing two different alcohol-radicles: they are obtained by distilling a salt of an acid diatomic ether with a salt of ethyl-sulphuric or an analogous acid (Chancel), *e.g.*:



The *neutral diatomic ethers of monatomic alcohol-radicles* are resolved by the action of *water*, or more quickly by that of a *caustic alkali*, into an alcohol and a salt of an acid ether, or into an alcohol and a salt of the corresponding acid:

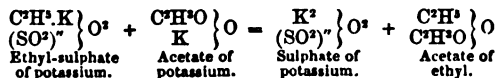


*Ammonia*, according to the proportion in which it is added, converts the diatomic ethers into an alcohol and an ether of an amic acid (an amethane), or into an alcohol and a diamide:

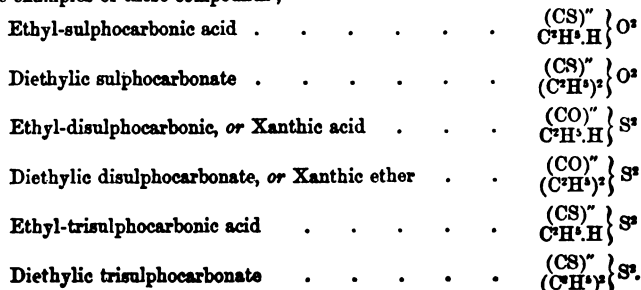


The *diatomic acid ethers of monatomic alcohol-radicles* are produced by heating the alcohols with certain dibasic acids, or by treating a neutral diatomic ether (oxalate of ethyl for example) with only half the quantity of alkali required to resolve it completely into acid and alcohol (see above).

These acid ethers in the free state are for the most part rather unstable, being easily resolved into acid and alcohol by boiling with water or with an alkali. Most of them are decomposed by distillation. They are monobasic acids, and form salts which are usually more stable than the acids themselves, and serve for the preparation of other ethers by double decomposition; *e.g.*:



The *sulphocarbonic ethers* are diatomic ethers, similar in constitution to those just described, but having the oxygen more or less replaced by sulphur. The following are examples of these compounds;



The disulphocarbonates, acid and neutral, of *methyl* and *amyl*, are known; also *cetyl*disulphocarbonic acid.

These ethers may also be regarded as compounds of carbonic anhydride, or of disulphide of carbon, with the protoxides, protosulphides, hydrates, or sulphhydrates of alcohol-radicles; e.g. *xanthic acid* =  $\text{CS}^2 \cdot (\text{C}^2\text{H}^3 \cdot \text{H} \cdot \text{O})$ ; *xanthic ether* =  $\text{CS}^2 \cdot (\text{C}^2\text{H}^3)^2\text{O}$ .

There are likewise ethers consisting of carbonic anhydride or disulphide of carbon combined with an alcoholic persulphide; e.g.

Ethyl-sulphocarbonic persulphide or Dicarboxate of ethylic persulphide  $\text{CO}^2 \cdot \text{C}^2\text{H}^3\text{S}$ .

Ethyl-disulphocarbonic persulphide or Dioxysulphocarbonate of ethyl  $\text{C}_2\text{H}_5\text{O} \cdot \text{C}_2\text{H}_5\text{O} \cdot \text{S}_2\text{O}_2$ .

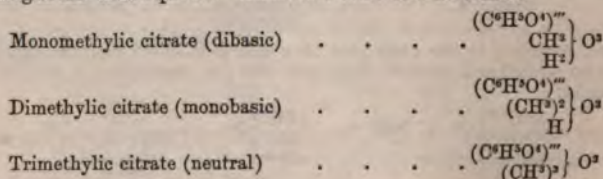
The *methyl*- and *amyl*-disulphocarbonic persulphides are also known.

For the formation and properties of all these compounds, see SULPHOCARBONIC ETHERS.

The chlorocarbonic ethers (i. 916), derived from the carbonic ethers by the substitution of an atom of chlorine for a molecule of the peroxide of an alcohol-radicle, e.g. *carbonate of ethyl* =  $(\text{CO}) \cdot \text{C}^2\text{H}^3\text{O} \cdot \text{C}^2\text{H}^3\text{O}$ ; *chlorocarbonate of ethyl* =  $(\text{CO}) \cdot \text{C}^2\text{H}^3\text{O} \cdot \text{Cl}$ , also belong to this place.

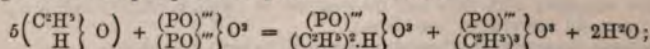
### c. Containing Triatomic Acid-radicles.

These ethers are derived from tribasic acids by the partial or total substitution of an alcohol-radicle for the basic hydrogen. Every tribasic acid is capable of forming three such ethers, which are dibasic, monobasic, or neutral, according as 1, 2, or 3 at. hydrogen are thus replaced. Thus from citric acid are formed

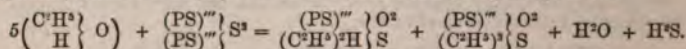


Ethers of aconitic, arsenic, boric, chelidonic, citric, cyanuric, meconic, phosphorous and phosphoric acids have likewise been obtained. The mode of formation and the reactions of these ethers are, for the most part, similar to those of the diatomic ethers (p. 515).

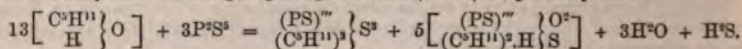
The diethylic and triethylic phosphates are produced simultaneously by heating alcohol with phosphoric anhydride in sealed tubes:



and in like manner, alcohol heated with sulphophosphoric anhydride (pentasulphide of phosphorus) yields diethylic and triethylic disulphophosphates:



A precisely similar reaction is obtained with *methylic alcohol* and the pentasulphide. With *amyllic alcohol*, however, the products are diamyllic disulphophosphate, and triamyllic tetrasulphophosphate,  $\text{PS} \cdot (\text{C}^5\text{H}^{11})^3\text{S}^3$ , probably thus:



All these sulphophosphoric ethers are oily, disagreeable-smelling liquids; the neutral ethers are insoluble, or nearly so, in water; the acid ethers soluble; they are all soluble in common alcohol and ether. The acid ethers form crystalline salts with metals. (Carius, Ann. Ch. Pharm. cxii. 190; Kovalévsky, *ibid.* cxix. 303.)

### 4. Haloïd Salts of Monatomic Alcohol-radicles.

The chlorides, bromides, &c., of these radicles may be regarded as formed from the alcohols by the substitution of Cl, Br, &c., for HO; e.g. *methylic alcohol*  $\text{CH}^3\text{HO}$ ; chloride of methyl  $\text{CH}^3\text{Cl}$ . They are produced by the action of the chlorides, bromides, and iodides of hydrogen, the metals, or phosphorus on the alcohols. They are mostly liquid at ordinary temperatures; chloride of methyl, however, is gaseous. They are decomposed by potash, especially in alcoholic solution, and by moist oxide of silver, yielding the corresponding alcohols, and a metallic



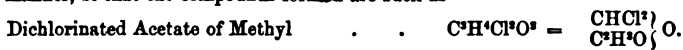
chloride, bromide, or iodide. They combine directly with ammonia and its basic derivatives, forming salts of amines.

Of the fluorides of the alcohol-radicles very little is known.

The alcoholic cyanides, or cyanhydric ethers, belong to the haloïd group, but differ considerably in their properties and in their modes of formation from the chlorides, bromides, and iodides.

For the particular properties of all these compounds see BROMIDES (i. 672), CHLORIDES (i. 897), CYANIDES (ii. 203), and IODIDES, of ALCOHOL-RADICLES.

*Chlorinated Oxygen-salts of Alcohol-radicles—Chloroconjugated Ethers.*—When chlorine is passed into a compound ether containing an alcohol-radicle of the ethyl-series,  $C^2H^{2n+1}$ , hydrochloric acid is evolved, and the hydrogen removed is replaced by chlorine, the action usually beginning with the substitution of 2 atoms of chlorine in this manner, so that the compounds formed are such as



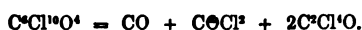
These dichlorinated ethers, when treated with alkalis, do not reproduce the alcohols, but exchange their 2 at. chlorine for 2 at. HO, derived from the alkaline hydrate, producing an alkaline chloride, the fatty acid corresponding to the alcohol from which the ether is derived, and the acid whose radicle is actually contained in the ether. Thus, either of the chlorinated ethers above mentioned yields with potash, chloride of potassium, formic acid, and acetic acid :



In short, either of these bodies acts with an alkali just like a dichloride of formyl and acetyl,  $\begin{matrix} CHO \\ C^2H^2O \end{matrix} \left\{ Cl^2.$

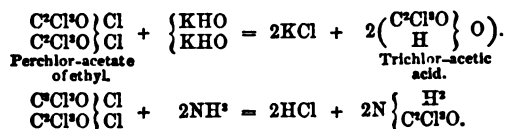
By the continued action of chlorine, especially in sunshine, the whole of the hydrogen contained in the ether is replaced by chlorine, and a perchlorinated ether is formed, such as perchlorinated acetate of ethyl,  $C^2Cl^4O^2 = \begin{matrix} C^2Cl^2 \\ C^2Cl^2O \end{matrix} \left\{ O. \right.$  When the action is somewhat less prolonged, or less energetic, intermediate products are formed.

The perchlorinated ethers, when decomposed by heat, caustic potash, or ammonia, split up into groups containing separately, the carbon belonging to the acid radicle, and that which belongs to the alcohol-radicle. *Perchlorinated oxalate of ethyl*, for example,  $(C^2O^2)^2 \left\{ O^2, \right.$  which may be regarded as  $\begin{matrix} (C^2O^2)^2 \\ (C^2Cl^2O)^2 \end{matrix} \left\{ Cl^4, \right.$  is resolved by heat into carbonic oxide, oxychloride of carbon (phosgene), and chloride of trichloracetyl (perchlorinated aldehyde) :



This last product ( $C^2Cl^4O$ ) is always obtained by the action of heat on the perchlorinated ethyl-ethers. *Perchlorinated acetate of ethyl*,  $\begin{matrix} C^2Cl^2 \\ C^2Cl^2O \end{matrix} \left\{ O, \right.$  or  $\begin{matrix} C^2Cl^4O \\ C^2Cl^2O \end{matrix} \left\{ Cl^2, \right.$  splits up at once into 2 at.  $C^2Cl^4O$ .

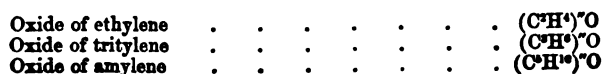
The same perchlorinated ethers, when decomposed by potash, always yield trichloroacetic acid ; and with ammonia, trichloroacetamide, *e. g.* :



### Ethers containing Diatomic Alcohol-radicles : Glycol-ethers.

#### 1. Oxides.

The three following have been obtained :—



These compounds are isomeric with the aldehydes of the fatty acids, *e. g.* oxide of ethylene with acetic aldehyde (i. 105).\*

Oxide of ethylene, produced by the action of potash on glycolic chlorhydrin  $(C^2H^4)^n.HO.Cl$ , is a very volatile liquid, possessing strong basic properties, and capable of uniting directly with a considerable number of bodies, *viz.* with hydrogen, oxygen, bromine, water, ammonia (Wurtz), and sulphydric acid (Foster). Its vapour-density shows that its molecule contains the same quantity of ethylene as the molecule of the corresponding alcohol  $(C^2H^4)^n.H^2O^2$ . In this respect it differs from the ethers of the monatomic alcohols, whose molecules contain twice as much of the alcohol-radicle as those of the alcohols themselves, *e. g.* ethylic alcohol =  $C^2H^5.H.O$ , ethylic ether =  $C^2H^5.C^2H^5.O$ .

The oxides of tritylene and amylenes are obtained in like manner, exhibit corresponding relations, and their molecules likewise contain the same quantity of the alcohol-radicles as the alcohols from which they are derived. It appears, then, that the ethers of both monatomic and diatomic alcohols are related to those alcohols in the same manner as the anhydrides of the monobasic and dibasic acids are related to those acids, thus :

Monatomic.		Diatomic.	
Ethylic alcohol.	Ethylic ether.	Ethylic alcohol.	Ethylic ether.
$\left. \begin{array}{c} C^2H^5 \\ H \end{array} \right\} O$	$\left. \begin{array}{c} C^2H^5 \\ C^2H^5 \end{array} \right\} O$	$\left( \begin{array}{c} C^2H^4 \\ H^2 \end{array} \right)^n O^2$	$(C^2H^4)^n O$ .
Acetic acid.	Acetic anhydride.	Sulphuric acid.	Sulphuric anhydride.
$\left. \begin{array}{c} C^2H^3O \\ H \end{array} \right\} O$	$\left. \begin{array}{c} C^2H^3O \\ C^2H^3O \end{array} \right\} O$	$\left( \begin{array}{c} SO^2 \\ H^2 \end{array} \right)^n O^2$	$(SO^2)^n O$ .

The molecule of a diatomic anhydride differs from that of the corresponding hydrate, by 1 at. water; thus:  $C^2H^4O^2 - H^2O = C^2H^4O$ ; and  $SH^2O^2 - H^2O = SO^2$ . In the corresponding monatomic compounds, this relation does not exist.

A body having the percentage composition of oxide of methylene,  $CH^2O$ , is obtained by the action of iodide of methylene on oxide or oxalate of silver, or of acetate of methylene on oxide of lead (Buttlerow); but it is not analogous to oxide of ethylene, for its vapour-density shows that its molecule contains 2 at. of methylene  $(CH^2)^2O^2$ . Moreover, it is a crystalline solid, much less volatile than oxide of ethylene, and apparently quite destitute of basic properties. It cannot, therefore, be regarded as the first term of the series of diatomic ethers  $(C^2H^4)^nO$ .

## 2. Oxygen-salts of Diatomic Alcohol-radicles.

These are the compound ethers of the glycols or diatomic alcohols, and may be derived from two (or  $2n$ ) molecules of water by the substitution of diatomic alcohol-radicles for one portion of the hydrogen, and of acid radicles for the remainder or for a portion of it. The following are examples of the formulæ:—

Diacetate of methylene (neutral)	. . . . .	$\left( \begin{array}{c} CH^2 \\ C^2H^3O \end{array} \right)^n O^2$
Monoacetate of ethylene (basic)	. . . . .	$\left( \begin{array}{c} C^2H^4 \\ C^2H^3O.H \end{array} \right)^n O^2$
Diacetate of ethylene (neutral)	. . . . .	$\left( \begin{array}{c} C^2H^4 \\ C^2H^3O \end{array} \right)^n O^2$
Aceto-butyrate of ethylene (neutral)	. . . . .	$\left( \begin{array}{c} C^2H^4 \\ C^2H^3O \\ C^4H^7O \end{array} \right)^n O^2$
Monoethylate of ethylene (basic)	. . . . .	$\left( \begin{array}{c} C^2H^4 \\ C^2H^3O \\ C^2H^5.H \end{array} \right)^n O^2$
Diethylate of ethylene (neutral)	. . . . .	$\left( \begin{array}{c} C^2H^4 \\ C^2H^5 \end{array} \right)^n O^2$
Oxalate of ethylene	. . . . .	$\left( \begin{array}{c} C^2H^4 \\ C^2O^4 \end{array} \right)^n O^2$

The following have likewise been obtained:—The *monobutyrate*, *monovalerate*, *dibuty-*

\* In the articles ALCOHOLS and ALDEHYDES (i. 103, 110). It is stated that the aldehydes are identical with the ethers of the diatomic alcohols: such indeed was the view entertained at the time when those articles were written; but subsequent researches have shown that the two groups of compounds are only isomeric.

rate, divalerate, aceto-valerate, distearate, and dibenzoates of ethylene; and the monoacetates of tritylene, tetrylene and amylenes; also several polyethylenic acetates of the general

formula,  $\left\{ \begin{smallmatrix} \text{C}^{\text{H}^*} \\ \text{C}^{\text{H}^*}\text{O} \end{smallmatrix} \right\}^{\text{O}^{n+1}}$ . Sulphocyanate of ethylene  $\left\{ \begin{smallmatrix} \text{C}^{\text{H}^*} \\ \text{C}_2 \end{smallmatrix} \right\}^{\text{S}^2}$ , may also be mentioned as analogous in constitution to the neutral ethers in the preceding table.

The compounds of benzylene,  $\text{C}^{\text{H}^*}$  (i. 577), are likewise analogous in composition to the glycol-ethers; but they are perhaps not strictly comparable therewith; for they are all formed by double decomposition from the chloride of benzylene  $(\text{C}^{\text{H}^*})^{\text{Cl}_2}$ , which is produced by the action of pentachloride of phosphorus on hydride of benzoyl. Now it is known that aldehyde (hydride of acetyl), treated with the same reagent, yields, not chloride of ethylene (Dutch liquid), but an isomeric body called chloride of ethylidene (i. 107). Hence it is probable that chloride of benzylene (chlorobenzol), and the compounds produced from it, are not true glycol-ethers. Similar observations apply to the compounds of allylene,  $\text{C}^{\text{H}^*}$  (i. 147).

The neutral ethers of diatomic alcohol-radicles are obtained by the action of silver-salts on the bromides or iodides of the corresponding alcohol-radicles, *e. g.*:



They are oily liquids, miscible in all proportions with common alcohol and ether; the acetates of methylene, ethylene, and tritylene are soluble in water, the rest are nearly or quite insoluble. They are easily decomposed by alkalis into a diatomic alcohol and a metallic salt of the acid.

### 3. Haloid Salts of Diatomic Alcohol-radicles.

The chlorides, bromides, &c., of these radicles may be derived from the diatomic alcohols in the same manner as the monatomic chlorides, &c., from their corresponding alcohols, viz. by the substitution of Cl, Br, &c., for an equivalent quantity of peroxide of hydrogen. But as there are 2 at. HO to be thus replaced, the substitution may be total or partial, producing in the one case a neutral, in the other a basic chloride, bromide, &c., *e. g.*:

Glycol	.	.	.	.	.	.	$(\text{C}^{\text{H}^*})^{\text{O}^2}.\text{HO}.\text{HO}$
Glycolic Chlorhydrin	.	.	.	.	.	.	$(\text{C}^{\text{H}^*})^{\text{O}^2}.\text{HO}.\text{Cl}$
Dichloride of Ethylene	.	.	.	.	.	.	$(\text{C}^{\text{H}^*})^{\text{O}^2}.\text{Cl}.\text{Cl}$

In the basic compounds, the remaining atom of hydrogen may be replaced by an acid radicle (or the remaining HO by the peroxide of an acid radicle), *e. g.*:

Glycolic Iodacetin	.	.	.	.	.	.	$(\text{C}^{\text{H}^*})^{\text{O}^2}.\text{C}^{\text{H}^*}\text{O}^2.\text{I}$
Glycolic Chlorobutylin	.	.	.	.	.	.	$(\text{C}^{\text{H}^*})^{\text{O}^2}.\text{C}^{\text{H}^*}\text{O}^2.\text{Cl}$

The dichlorides, &c., of the diatomic alcohol-radicles are produced by the direct combination of these radicles with chlorine, bromine, and iodine, or by the action of perchloride or bromide of phosphorus on the corresponding diatomic alcohols or their basic haloid salts. The first mentioned reaction is characteristic of the diatomic alcohol-radicles, and serves to separate those which are gaseous from mixtures of gases and vapours in which they occur. Most of these compounds are oily liquids; but iodide of ethylene and its higher homologues are solid at common temperatures. Alcoholic potash converts them into the chlorides of monatomic radicles.

The basic haloid compounds of ethylene are oily liquids, whose reactions are similar to those of the monatomic alcoholic chlorides, bromides, &c.; but when treated with alkalis, they yield the corresponding diatomic oxides (p. 517).

### Ethers containing Triatomic Alcohol-radicles.

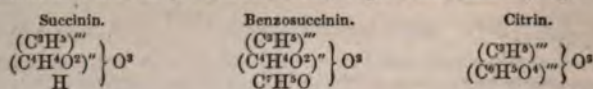
The only compounds of this group at present known are the glycerides, which are derived from a molecule of glycerin,  $\left\{ \begin{smallmatrix} \text{C}^{\text{H}^*} \\ \text{H}^2 \end{smallmatrix} \right\}^{\text{O}^3}$ , by the substitution of acid radicles for 1, 2, or 3 at. hydrogen, *e. g.*:

Monostearin.	Distearin.	Tristearin.
$\left\{ \begin{smallmatrix} \text{C}^{\text{H}^*} \\ \text{C}^{18}\text{H}^{32}\text{O} \end{smallmatrix} \right\}^{\text{O}^3}$	$\left\{ \begin{smallmatrix} \text{C}^{\text{H}^*} \\ \text{C}^{18}\text{H}^{32}\text{O} \end{smallmatrix} \right\}^{\text{O}^3}$	$\left\{ \begin{smallmatrix} \text{C}^{\text{H}^*} \\ \text{C}^{18}\text{H}^{32}\text{O} \end{smallmatrix} \right\}^{\text{O}^3}$

These glycerides are produced by heating glycerin with the respective acids in sealed tubes in the required proportions. Most of those which have hitherto been formed contain only monatomic acid radicles; many of those in which 3 at. hydrogen are thus replaced, exist as natural fats.

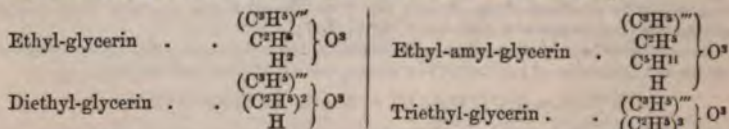


A few glycerides have also been formed containing diatomic and triatomic, as well as monatomic acid radicles (Van Bemmelen, J. pr. Chem. lxi. 84), *e. g.* :



All these glycerides are oily liquids or solid fats, which, when boiled with alkalis, are resolved into glycerin and an alkali-salt of the acid contained in them. This is the reaction which takes place in the ordinary process of soap-making or saponification.

Glycerides are also known containing monatomic alcohol-radicles, *e. g.* :

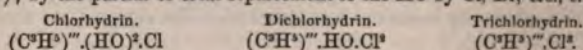


For the preparation and properties of these compounds, see GLYCERIDES.

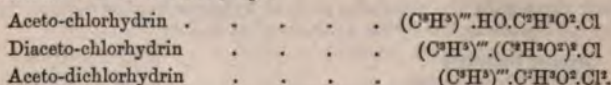
Berthelot obtained oxide of glyceryl, or glyceric ether,  $\left\{ \begin{array}{c} (C^2H^3)^{''' } \\ (C^3H^3)^{'' } \end{array} \right\} O^3$ , by the action of potash upon iodhydric.

The triatomic haloïd-compounds of the alcohol-radicles resemble the corresponding diatomic compounds (p. 518) in their constitution and many of their properties.

The haloïd-compounds of glycerin are obtained by heating that liquid with hydrochloric, hydrobromic acid, &c., in sealed tubes. They are derived from glycerin,  $C^3H^5.(HO)^3$ , by the partial or total replacement of the HO by Cl, Br, &c., *e. g.* :

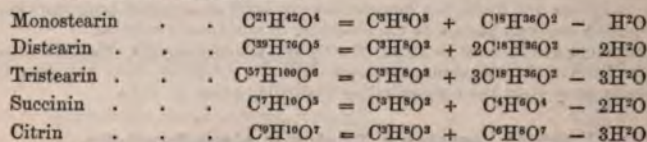


By heating glycerin with a mixture of hydrochloric acid, &c., and an oxygen-acid, similar compounds are obtained, in which the HO is replaced partly by Cl, &c., partly by the peroxide of an acid radicle, *e. g.* :

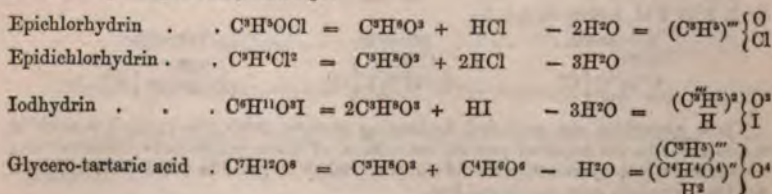


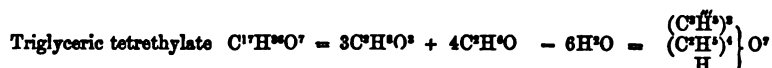
These ethers are oily liquids which, when boiled with alkalis, reproduce the acid or acids and glycerin.

The formation of all the glycerides above mentioned is attended with the elimination of a number of atoms of water equal to the number of atoms of a monobasic acid, or double that number of a dibasic acid, or three times that number of a tribasic acid, which enter into the combination, thus :



See also page 509. There are, however, a number of glycerides whose formation is attended with the elimination of a number of atoms of water greater or less than that indicated by the preceding rule, *e. g.* :



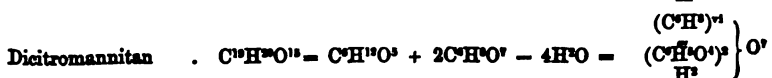
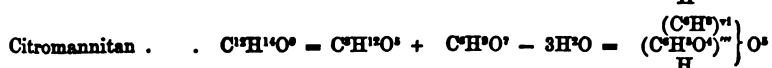
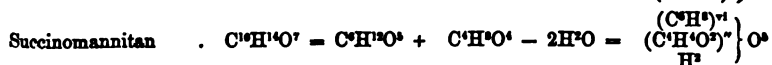
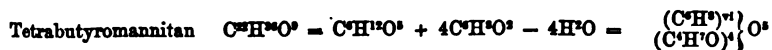
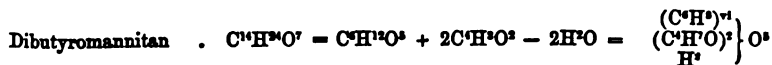
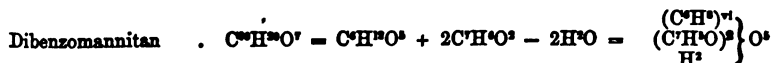
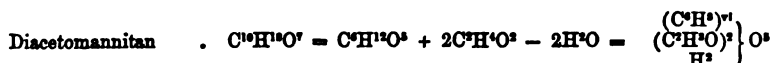
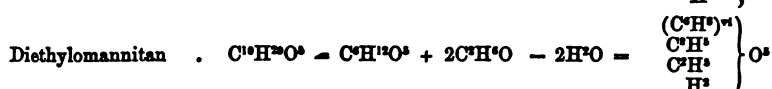


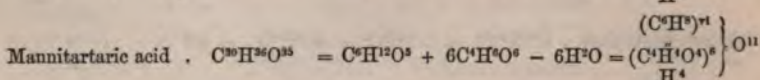
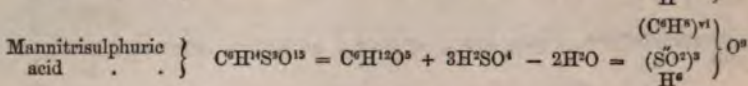
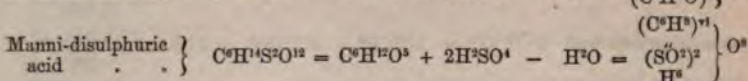
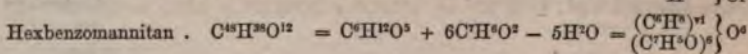
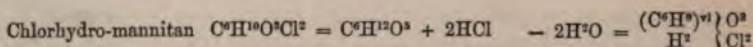
#### Ethers containing Tetratomic Alcohol-radicles.

The only known ethers of this class are the erythromannitic ethers (p. 505), derived from the tetratomic alcohol,  $\left\{ \begin{array}{c} (\text{C}^4\text{H}^4)^{\text{IV}} \\ \text{H}^2 \end{array} \right\} \text{O}^4$ , e. g. the dibenzoate,  $(\text{C}^6\text{H}^5\text{O})^2\text{H}^2$  O<sup>4</sup>; the mono-orsellate (picroerythrin) =  $\left\{ \begin{array}{c} (\text{C}^4\text{H}^4)^{\text{IV}} \\ \text{C}^6\text{H}^5\text{O}^2\text{H}^2 \end{array} \right\} \text{O}^4$ .

#### Ethers containing Hexatomic Alcohol-radicles.

The mannitanides and dulcitanides belong to this group, being derived from mannitan or dulcitan, C<sup>6</sup>H<sup>12</sup>O<sup>6</sup>, which is a tetratomic alcohol, containing the hexatomic radicle C<sup>6</sup>H<sup>6</sup>, thus:

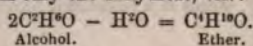




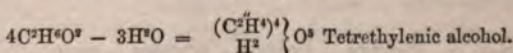
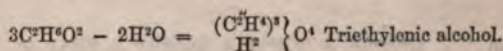
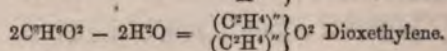
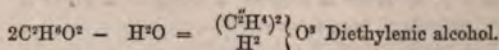
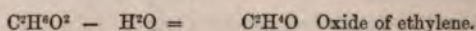
The dulcitanides have the same composition as the mannitanides. At page 348 they are represented as derived from a tetratomic alcohol, dulcitan,  $\left( \frac{C^6H^9O}{H^2} \right)^4 \left\{ O^4 \right.$ , containing an oxygenated radicle. This supposition is somewhat inconsistent with the nature of alcohols in general: and it is better to derive these compounds, as above, from an alcohol containing the hexatomic radicle  $C^6H^9$ . In fact, Wanklyn and Erlenmeyer have shown (*Rép. Chim. pure* 1862, p. 361; *Chem. Soc. J.* xv. 456) that mannite and dulcite,  $C^6H^{10}O^6$ , are hexatomic, their rational formula being  $\left( \frac{C^6H^9}{H^6} \right)^2 \left\{ O^6 \right.$ ; and from this formula that of mannitan (and dulcitan),  $\left( \frac{C^6H^9}{H^4} \right)^2 \left\{ O^5 \right.$ , is derived by simple elimination of water. As this formula contains 4 at. replaceable hydrogen, the molecule, considered as an alcohol, is still tetratomic.

#### Polyethylenic, Polyglyceric Ethers, &c.

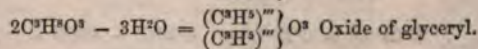
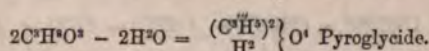
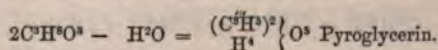
The polyatomic alcohols differ from the monatomic alcohols in this respect, that they are capable of undergoing dehydration in various degrees. Common alcohol, which is monatomic, can form only one anhydride, viz.:



But glycol, which is diatomic, is capable of forming an indefinite number of anhydrides, *e. g.*:



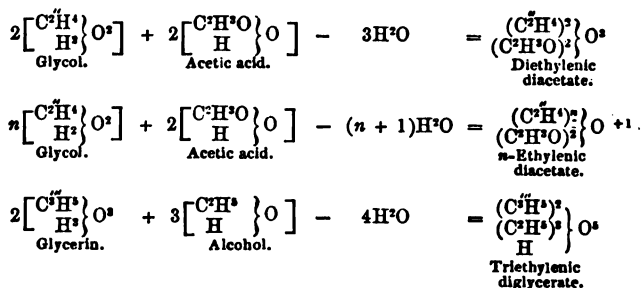
Glycerin, in like manner, forms polyglyceric alcohols, thus:



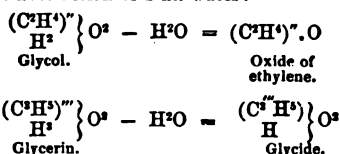
All these compounds may be regarded as ethers, inasmuch as, like common ether, they are formed by the union of two or more molecules of an alcohol, with elimination of water, but those which still contain replaceable hydrogen are usually regarded as alcohols.



When, in such an equation as the above, a molecule of a polyatomic alcohol is replaced by one or more molecules of an acid, compound ethers result, of different atomicity from the alcohol from which they are derived: *e. g.*—



A single molecule of a di- or tri-atomic alcohol can undergo only one degree of dehydration; viz. by the abstraction of 1 at. water:



But a single molecule of an alcohol of higher atomicity may undergo several degrees of dehydration. Thus, from mannite,  $\left( \begin{array}{c} \text{C}^{\text{H}^3} \\ \text{H}^2 \end{array} \right) \text{O}^2$ , there are formed by successive abstraction of  $\text{H}^2\text{O}$ , the compounds *mannitan*,  $\left( \begin{array}{c} \text{C}^{\text{H}^3} \\ \text{H}^2 \end{array} \right)^{\text{r}} \text{O}^2$ , *mannide*,  $\left( \begin{array}{c} \text{C}^{\text{H}^3} \\ \text{H}^2 \end{array} \right)^{\text{r}} \text{O}^2$ , and the theoretically possible *oxide of mannityl*,  $(\text{C}^{\text{H}^3})^{\text{r}} \text{O}^2$ .

**ETHERS, ACETIC.** These and the ethers of other oxygen-acids are described after the several acids.

**ETHERS, BROMHYDRIC or HYDROBROMIC.** These and the ethers of other halogen-acids are described under the several alcohol-radicles, *ALLYL*, *AMYL*, *ETHYL*, &c.

**ETHIDE, BORIC.** See *ETHYL*, BORIDE OF (p. 526).

**ETHIONIC ACID.**  $\text{C}^{\text{H}^4}\text{S}^2\text{O}^2 = \text{C}^{\text{H}^4}.2\text{SO}^2.\text{H}^2\text{O}$ . (Magnus, Pogg. Ann. xxvii. 378; xlvii. 514.—Marchand, *ibid.* xxxii. 466.)—Produced by the action of water on ethionic anhydride; also by saturating anhydrous alcohol or ether with sulphuric anhydride and diluting with water. Or the barium-salt may first be prepared by adding absolute alcohol to ethionic anhydride, then diluting with water and saturating with carbonate of barium, evaporating the filtrate at  $100^\circ \text{C}$ . till precipitation commences, and completing it by addition of absolute alcohol; and from the barium-salt the acid may be obtained by precipitating the barium with dilute sulphuric acid. The aqueous acid cannot be evaporated without decomposition, even in *vacuo*, as it splits up into sulphuric and isethionic acids:



At the boiling heat this change takes place rapidly.

The ethionates appear to contain, in the dry state,  $\text{C}^{\text{H}^4}\text{M}^{\text{r}}\text{S}^2\text{O}^2$ , the acid being dibasic. The ammonium-, potassium-, sodium-, and barium-salts crystallise readily. The *potassium-salt*,  $\text{C}^{\text{H}^4}\text{K}^{\text{r}}\text{S}^2\text{O}^2 + \frac{1}{2}\text{H}^2\text{O}$ , does not give off any water in *vacuo*, or even when heated, before decomposition takes place. At a high temperature, it blackens and yields a sublimate of sulphur. Heated with hydrate of potassium, it yields sulphate and sulphite of potassium. The *barium-salt*,  $\text{C}^{\text{H}^4}\text{Ba}^{\text{r}}\text{S}^2\text{O}^2 + \text{H}^2\text{O}$ , gives off  $\frac{1}{2}$  at. water in *vacuo*, and decomposes at  $100^\circ \text{C}$ . Heated in a tube, it yields a sublimate of sulphur. It dissolves in about 10 pts. of water at  $20^\circ \text{C}$ .

**ETHIONIC ANHYDRIDE.** *Sulphate of Carbyl*,  $\text{C}^{\text{H}^4}.2\text{SO}^2$  (Regnault, Ann. Ch. Phys. lxx. 98; Magnus, Pogg. Ann. xlvii. 509), is obtained by bringing together olefiant gas and vapour of sulphuric anhydride in a tube; also when absolute alcohol is left for some time exposed to the vapour of sulphuric anhydride. It forms crystals, which melt at  $80^\circ \text{C}$ ., and deliquesce in the air. They mix with water

and alcohol, producing rise of temperature, and yielding a solution of ethionic acid. If, however, the heat produced by the reaction is very great, isethionic acid is likewise produced.

Ethionic anhydride and ethionic acid may be represented typically as follows:

Type.	Ethionic anhydride.	Type.	Ethionic acid.
$\text{H}^2$	$\left\{ \text{C}^2\text{H}^4 \right\} \text{O}$	$\text{H}^2$	$\left\{ \text{H}^2 \right\} \text{O}$
$\text{H}^2\text{O}$	$\left\{ \text{SO}^2 \right\} \text{O}$	$\text{H}^2\text{O}$	$\left\{ \text{C}^2\text{H}^4 \right\} \text{O}$
$\text{H}^2\text{O}$	$\left\{ \text{SO}^2 \right\} \text{O}$	$\text{H}^2\text{O}$	$\left\{ \text{SO}^2 \right\} \text{O}$
		$\text{H}^2\text{O}$	$\left\{ \text{SO}^2 \right\} \text{O}$

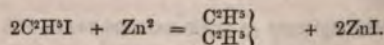
**ETHYL.**  $\text{C}^2\text{H}^3$ , often denoted by the shorter symbol, E; in the free state,  $\text{C}^2\text{H}^{10} = \text{E}^2$ . — The radicle of ordinary alcohol and ether. It was first obtained in the free state by Frankland in 1849 (Chem. Soc. Qu. J. ii. 263). It is produced from iodide of ethyl by the action of zinc at high temperatures; also by the action of light.

*Preparation.*—1. Pure iodide of ethyl is heated with finely divided zinc in a strong sealed glass tube immersed in an oil-bath. The granulated zinc is first introduced into the tube; the upper extremity of the tube then drawn out and bent twice at right angles; the iodide is introduced by heating and afterwards cooling the tube, while its open extremity dips into the liquid; the air is then exhausted by the air-pump; and the tube is sealed and immersed in an oil-bath. The decomposition of the iodide of ethyl begins at about  $100^\circ \text{C}$ .; white crystals are deposited on the glass (probably consisting of a compound of iodide of zinc and zinc-ethyl), together with a colourless mobile liquid, equal in bulk to about half the iodide of ethyl used, and consisting of condensed ethyl, hydride of ethyl, and ethylene. These compounds are separated by their different degrees of volatility. The tube when cold is immersed in a mixture of ice and salt, and the narrow end is broken off under water.

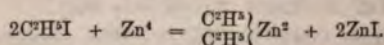
The ethylene and hydride of ethyl being more volatile than the ethyl itself, escape in greatest abundance when the tube is first opened; and by collecting apart the gas which comes over after the evolution has become slow and regular, a gas is obtained, which, when freed from ethylene and undecomposed iodide of ethyl by means of sulphuric anhydride, and from sulphurous acid by potash, is found to be pure ethyl,  $\text{C}^2\text{H}^{10}$ .

In the preceding reaction three distinct chemical changes occur, viz.:

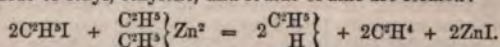
i. The decomposition of iodide of ethyl by zinc, with formation of ethyl and iodide of zinc:



ii. The decomposition of iodide of ethyl by zinc, with formation of zinc-ethyl and iodide of zinc:



iii. The reaction of the zinc-ethyl thus formed on the undecomposed iodide of ethyl, by which hydride of ethyl, ethylene, and iodide of zinc are formed:



2. A few drops of iodide of ethyl are introduced into an inverted glass globe filled with mercury and exposed to sunshine; or, better, the sun's rays are concentrated on the iodide of ethyl at the top of the mercury by a parabolic mirror. The iodide of ethyl is then decomposed, iodide of mercury is formed, and the globe becomes filled with gas, which is a mixture of ethyl, hydride of ethyl, and ethylene, the two latter being produced by the decomposition of a portion of the ethyl:  $\text{C}^2\text{H}^{10} = \text{C}^2\text{H}^6 + \text{C}^2\text{H}^4$ . In this process, however, only one-fifth of the ethyl is thus decomposed, whereas in the decomposition by zinc, the quantity thus lost is about one-third of the whole. The ethyl is freed from the other two gases as in the preceding process. (Frankland, Ann. Ch. Pharm. lxxvii. 221.)

Ethyl is at ordinary temperatures a colourless gas, having a slightly ethereal odour (if perfectly pure, it would probably be inodorous); it burns with a white and very luminous flame. Its specific gravity was found by a diffusion-experiment, according to Graham's law (see GASES, DIFFUSION OF), to be 2.0. This shows that its molecule in the gaseous state is represented by the formula  $\text{C}^2\text{H}^{10}$ ; for  $\frac{4.12 + 10.1}{2} \times 0.0693 = 2.009$  (see ALCOHOL-RADICLES, i. 97). It does not condense at  $-18^\circ \text{C}$ . ( $0^\circ \text{Fah.}$ ); but in an Oerstedt's condensing apparatus, it condenses at  $+3^\circ$ , and under a pressure of  $2\frac{1}{2}$  atmospheres, to a transparent, colourless, very mobile liquid: hence its boiling point under the ordinary pressure is probably about  $-23^\circ \text{C}$ .

Ethyl is nearly insoluble in water, but soluble in absolute alcohol. 1 vol. absolute alcohol at 14.2° C., and under a pressure of 744.8 mm. dissolves 18.13 vol. of the gas, but gives it up again on the addition of a small quantity of water. (See GASES, ABSORPTION OF.)

1 vol. ethyl-gas (containing  $C^2H^4$ ) requires  $6\frac{1}{2}$  vol. oxygen to burn it completely: for 5 at. or 5 vol. H require  $2\frac{1}{2}$  vol. O, and 2 at. C require 4 at. (or 4 vol.) O. The products of the combustion are water and 4 vol.  $CO^2$ . Mixed with half its volume of oxygen, and passed over spongy platinum, it remains unaltered at ordinary temperatures; but on the application of a gentle heat, the platinum becomes red-hot, a small quantity of charcoal is deposited, and water, together probably with marsh-gas, produced. It is not acted upon by *nitric, chromic, or fuming sulphuric acid*. With *iodine and sulphur* it does not combine even when moderately heated; but at a red heat, sulphuretted hydrogen is formed, and charcoal separated. *Chlorine* does not act upon ethyl in the dark; but a dry mixture of the two gases in equal volumes, exposed to diffused light, undergoes a change of volume and forms a colourless liquid. *Bromine* acts upon ethyl when the two are gently heated together in the direct rays of the sun, but the products of the decomposition have not yet been examined.

Ethyl enters into the composition of a large number of compounds, in which it plays the part of a monatomic basylous radicle, analogous to hydrogen or potassium, so that the chloride, bromide, nitrate, acetate, &c., contain 1 at.  $C^2H^3$ ; the oxide, sulphide, neutral sulphate, and other neutral ethyl-salts of dibasic acids contain 2 at.  $C^2H^2$ ; the neutral salts of tribasic acids, such as the phosphate or cyanurate, 3 at.  $C^2H^2$ , &c. &c. It likewise unites with other alcohol-radicles, viz. tetryl and amyl, producing compound alcohol-radicles, which, in their constitution and mode of formation, are exactly analogous to ethyl itself, regarded as  $C^2H^3.C^2H^3$ . (See ALCOHOL-RADICLES, i. 97.)

**ETHYL-AMYL.**  $C^2H^{10} = C^2H^3.C^2H^7$ . (Wurtz, Ann. Ch. Phys. [3] xlv. 275.)—This compound is obtained by decomposing 60 pts. of iodide of ethyl and 70 pts. of iodide of amyl with 14 pts. of sodium in a flask provided with an upright condensing tube cooled by ice-cold water, so that the condensed vapours may run back into the flask. The action begins in the cold, and is attended with evolution of heat; towards the end, however, it requires to be sustained by external heating. The action is then kept up by adding quantities of the materials about equal to the former, and when it is complete, the product is distilled in an oil-bath, the portion which goes over below 120° C. being collected apart, and heated to 120° with excess of sodium in a sealed tube to complete the decomposition. By fractional distillation of the products, ethyl-amyl is obtained as a liquid boiling at 88° C., of specific gravity 0.7069 at 0°, and vapour-density = 3.522, corresponding with a condensation to two volumes  $\left(\frac{7.12 + 16.1}{2} \times 0.0693 = 3.465\right)$ . It is but slightly attacked by pentachloride of phosphorus at its boiling point; but in sealed tubes decomposition takes place: the products have not, however, been examined.

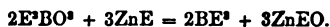
**ETHYL-TETRYL.**  $C^2H^{14} = C^2H^3.C^2H^7$ . (Wurtz, loc. cit.)—Prepared, like the preceding compound, by decomposing 40 grms. iodide of tetryl, and 34 grms. iodide of ethyl with 11 grms. sodium. It is a mobile liquid, boiling at 62° C., of specific gravity 0.7011 at 0°, and vapour-density = 3.053 (calc.  $\frac{6.12 + 14.1}{2} \times 0.0693 = 2.980$ ).

The compounds of ethyl with oxygen, sulphur, chlorine, bromine, and other elementary bodies, will be described here in alphabetical order; the oxygen-salts, such as the acetate, benzoate, &c., are described after the corresponding acids.

**ETHYL, ANTIMONIDES OF.** *Antimonethyle, Stibethyle, Ethylstibines.* See ANTIMONY-RADICLES, ORGANIC, i. 339.

**ETHYL, ARSENIDES OF.** *Arsenethyle, Ethylarsines.* See ARSENIC-RADICLES, ORGANIC, i. 397.

**ETHYL, BORIDE OF.** *Boric Ethide, Borethyl.*  $C^2H^3B = B(C^2H^3)^3 = BE^3$ . (Frankland, Phil. Trans. 1862, p. 167; Chem. Soc. J. xv. 363.)—Produced by the action of zinc-ethyl on triethyl borate (i. 650):\*



*Preparation.*—Several ounces of boric ether were placed in a capacious flask closed

\* Frankland prepares triethyl borate by distilling about 3 lbs. of a mixture of 2 pts. dried borax and 3 pts. ethylsulphate of potassium in a Papin's digester; agitates the crude distillates from several such operations, consisting of boric ether and a large excess of alcohol, with fused chloride of calcium to remove the latter; decants the upper layer of liquid thus produced, which consists of boric ether, with only a little alcohol, from the alcoholic solution of chloride of calcium below it; and subjects it to distillation, collecting the liquid which passes over between 118° and 123° C.



by a doubly perforated cork. Through one of the perforations passed a thermometer, and through the other a short glass tube, one fourth of an inch in diameter, and open at both ends: the bulb of the thermometer dipped into the boric ether. Successive quantities of pure zinc-ethyl were introduced through the short glass tube by means of a pipette, the elevation of temperature after each addition being allowed to subside before the next portion was added. The failure of a further addition of zinc-ethyl to produce any rise of temperature was regarded as evidence of the completion of the reaction, which was not attained until a comparatively very large amount of zinc-ethyl had been added.

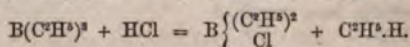
The liquid in the flask was now submitted to distillation in an oil-bath. It began to boil at  $94^{\circ}\text{C}.$ , and between this temperature and  $140^{\circ}\text{C}.$  a considerable quantity of a colourless liquid distilled over. The distillation then suddenly stopped, and, to avoid secondary products of decomposition by the application of a greater heat, the operation was interrupted. On cooling, the materials remaining in the flask solidified to a mass of large crystals of ethylate of zinc and zinc-ethyl. On rectification, the distillate began to boil at  $70^{\circ}\text{C}.$ , but the thermometer rose rapidly to  $95^{\circ}$ , at which temperature the last two-thirds of the liquid passed over and were received apart. The product thus collected exhibited a constant boiling-point on re-distillation.

*Properties.*—Borethyl is a colourless mobile liquid having a pungent odour; its vapour is very irritating to the mucous membrane, and provokes a copious flow of tears. The specific gravity of borethyl at  $23^{\circ}\text{C}.$  is 0.6961; it boils at  $95^{\circ}\text{C}.$  Its vapour-density, as determined by Gay-Lussac's method, is 3.4006; by calculation, for a condensation to two volumes, it is  $3.396 \left( = \frac{11 + 6.12 + 15.1}{2} \times 0.0693 \right)$ .

The density of borethyl vapour increases more considerably than is usual, as the temperature approaches the boiling-point; thus a determination made at  $132^{\circ}\text{C}.$  gave the number 3.6979, whilst a second showed the specific gravity of the vapour at  $101.6^{\circ}\text{C}.$  to be no less than 3.757.

Borethyl is insoluble in water, and is very slowly decomposed by prolonged contact with it. Iodine has scarcely any action upon it, even at  $100^{\circ}\text{C}.$  It floats upon concentrated nitric acid for several minutes without change; but suddenly a violent reaction takes place, and crystals of boric acid separate. When borethyl vapour comes in contact with air, it produces slight bluish-white fumes, which in the dark are seen to proceed from a lambent blue flame. The liquid is spontaneously inflammable in air, burning with a beautiful green and somewhat fuliginous flame. In contact with pure oxygen it explodes. Excluded from the air, borethyl is quite a stable body; a quantity of it kept in a sealed tube for two years exhibited, on examination, no evidence of alteration.

When borethyl is heated to  $99^{\circ}\text{C}.$  with strong hydrochloric acid over mercury, a considerable quantity of hydride of ethyl is slowly evolved, and chloroborethyl is formed:



When borethyl is heated with water to  $99^{\circ}\text{C}.$  for several hours, it also appears to suffer an analogous decomposition, although with extreme slowness; even with hydrochloric acid, the action is very tedious. In the cold, a strong solution of hydrofluoric acid has no action upon borethyl, which also suffers scarcely any change by being heated to  $99^{\circ}\text{C}.$  for four hours with concentrated sulphuric acid. Gently heated for fourteen days with sodium in a sealed tube, borethyl underwent no visible change.

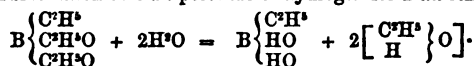
*Ammonio-Borethyl*,  $\text{NH}_2\text{B}(\text{C}^2\text{H}^5)^3$ .—When a few drops of borethyl are passed up into a dry eudiometer filled with mercury, and dry ammoniacal gas is admitted into the same tube, each bubble of gas collapses with a shock, like that produced by a bubble of steam projected into cold water. A large quantity of ammonia is thus absorbed by borethyl with extreme energy. To prepare the compound thus formed in larger quantity, several grammes of borethyl were placed in a small flask filled with nitrogen and surrounded with ice; a current of dry ammoniacal gas was now passed into the flask as long as it was absorbed; finally, the product thus obtained was warmed to expel excess of ammonia, and then exposed in vacuo over sulphuric acid for twenty-four hours. It did not crystallise, and could not be distilled, except in vacuo, without decomposition.

Ammonio-borethyl is a somewhat oily liquid, possessing an aromatic odour and an alkaline reaction. Carbonic acid has no action upon it, even in presence of water, but ether acids decompose it instantly and liberate borethyl. When it is exposed to a measured quantity of atmospheric air, there is scarcely any perceptible absorption of oxygen, even after the lapse of several hours.

*Oxide of Borethyl*,  $B(C^2H^5)_2O = B \begin{Bmatrix} C^2H^5 \\ C^2H^5O \\ C^2H^5O \end{Bmatrix}$ .—When borethyl is placed in a

flask and allowed to oxidise gradually, first in dry air and finally in dry oxygen, it forms a colourless liquid, which boils at  $125^\circ C$ , but cannot be distilled under atmospheric pressure without partial decomposition. At the ordinary temperature, this product of oxidation evaporates without residue in a stream of carbonic anhydride. It can be distilled in vacuo without decomposition.

This body, which is the oxide of borethyl, may be regarded, as shown by the second of the above formulae, as dioxethylo-borethyl, i.e. as borethyl in which 2 at. ethyl are replaced by 2 at. peroxide of ethyl; and this view of its constitution is supported by its behaviour with water: for when placed in contact with water, it is instantly decomposed, yielding alcohol and dioxhydro-borethyl, a compound derived from borethyl by the substitution of 2 at. peroxide of hydrogen for 2 at. ethyl:



Dioxhydro-borethyl may be conveniently prepared in the pure state by agitating its aqueous solution with ether, which dissolves the boric compound. The ethereal solution must then be decanted; and on evaporation at common temperatures in a stream of carbonic anhydride, the compound is left behind as a white and very volatile crystalline mass, very soluble in water, alcohol, and ether. It has an agreeable ethereal odour, and a most intensely sweet taste. Exposed to the air it evaporates at ordinary temperatures, undergoing at the same time partial decomposition, and invariably leaving a slight residue of boric acid. It may be sublimed without change at about  $40^\circ C$ . in a current of carbonic anhydride, and then condenses in magnificent crystalline plates resembling naphthalin. It melts at a gentle heat, and at a higher temperature boils with partial decomposition. Its vapour tastes intensely sweet. It reddens litmus, but does not appear to be capable of forming definite salts with metallic bases; oxide of borethyl may, however, as already observed, be regarded as its ethyl-salt.

Frankland gives also another view of the composition of these bodies. He regards borethyl as boric anhydride,  $BO^2$  or  $B^2O^3$ , in which the whole of the oxygen is replaced by an equivalent quantity of ethyl (1 at.  $C^2H^5$  for each at.  $O = 8$ , or 2 at.  $C^2H^5$  for each at.  $O = 16$ ), and supposes that when this compound is exposed to the action of the air or of oxygen gas, 2 at. ethyl are removed, and their place supplied by an

equivalent quantity of oxygen, producing *dioxyborethyl*, or *boric dioxethide*,  $B \begin{Bmatrix} C^2H^5 \\ O \\ O \end{Bmatrix}$ , or

$B \begin{Bmatrix} C^2H^5 \\ O^2 \end{Bmatrix}$ , which remains combined with the oxide of ethyl formed at the same time,

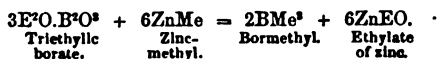
producing *diethylate of boric dioxethide*,  $B \begin{Bmatrix} C^2H^5 \\ O^2 \end{Bmatrix} . (C^2H^5)_2O$ , or  $B \begin{Bmatrix} C^2H^5 \\ C^2H^5O \\ C^2H^5O \end{Bmatrix}$ ; and this,

when subjected to the action of water, yields *dihydrate of boric dioxethide*,

$B \begin{Bmatrix} C^2H^5 \\ HO \\ HO \end{Bmatrix} . H^2O$ , or  $B \begin{Bmatrix} C^2H^5 \\ HO \\ HO \end{Bmatrix}$ , which may be regarded as a dibasic acid, of which the hy-

pothetical compound,  $B \begin{Bmatrix} C^2H^5 \\ O^2 \end{Bmatrix}$ , is the anhydride.

An argument in favour of the supposition that borethyl is produced by the substitution of ethyl for oxygen in boric anhydride, is deduced from the formation of the analogous compound, bormethyl, or boric methide,  $B(CH^3)_2$ , or  $BMe^2$ , by the action of zinc-methyl on triethyllic borate, which takes place as shown by the equation:



Here the methyl evidently goes to the boron and the oxygen to the zinc; whereas if, as supposed by Kekulé (*Lehrbuch*, p. 489), the action consisted in a simple deoxidation of the boric ether, the products would be methylate of zinc,  $ZnMeO$ , and borethyl,  $BE^2$ : hence it may be inferred that the decomposition of boric ether by zinc-ethyl is likewise, not a mere deoxidation of the former, but a process of substitution. It must be observed, however, that the interchange which takes place in the formation of the methyl-compound is not that of methyl for oxygen, but of methyl for peroxide of ethyl,  $EO$ , the reaction being most clearly represented in the form:





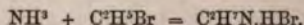
Moreover, Frankland finds that zinc-ethyl has no action whatever on boric anhydride at any temperature to which a mixture of the two may be exposed. This may indeed be due to the insolubility of the boric anhydride in the zinc-ethyl; but it may also indicate that the association of an alcohol-radicle with the boron is an essential condition of the reaction.

**ETHYL, BROMIDE OF.**  $C^2H^5Br$ . *Hydrobromic or Bromhydric Ether*. (Serullas, Ann. Ch. Phys. xxxiv. 99.—Löwig, Ann. Ch. Pharm. iii. 291.)—Discovered by Serullas in 1827. Produced by the action of bromine, hydrobromic acid, or bromide of phosphorus, on alcohol.

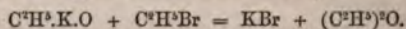
*Preparation*.—1. One part of phosphorus and 40 pts. of alcohol of  $38^\circ$  Bm. are introduced into a tubulated retort, and 7 to 8 pts. of bromine gradually added, whereupon the mixture becomes heated and hydrobromic and phosphorous acids are produced; the tubulus is then closed, the mixture distilled at a gentle heat, the distillate collected in a cooled receiver, and the hydrobromic ether separated from it by water, to which, if the distillate contains acid, a small quantity of potash is added (Serullas).—2. Absolute alcohol gradually mixed in a distillatory apparatus with a treble quantity of bromine and heated from without towards the end of the process, yields a distillate consisting of two layers. The lower reddish stratum, which consists of bromide of ethyl, a small quantity of bromide of carbon ( $C^2Br^4$ ), and free bromine, is freed from the latter by agitation with dilute potash till it loses its colour, and then from bromide of carbon by distillation (Löwig).—3. According to De Vrij, it is easily prepared by distilling 4 pts. pulverised bromide of potassium with 5 pts. of a mixture of 2 pts. strong sulphuric acid and 1 pt. alcohol of 96 per cent.

*Properties*.—Transparent and colourless liquid, heavier than water (Serullas). Specific gravity 1.40 (Löwig); 1.4733 at  $0^\circ$  (Pierre). Vapour-density = 3.754 (R. Marchand, J. pr. Chem. 188). Very volatile. Boiling point  $40.7^\circ C.$ , when the barometer stands at 757 mm. (Pierre). Has a strong ethereal odour and a pungent taste (Serullas). According to Löwig, its taste is strongly and disagreeably sweetish, with a somewhat burning after-taste. The vapour, when inhaled, exerts an anæsthetic action, like chloroform (Robin, Compt. rend. xxxii. 649). It is sparingly soluble in water, but mixes in all proportions with alcohol and ether.

*Decompositions*.—1. Vapour of hydrobromic ether passed through a glass tube at a low red heat is resolved into ethylene and hydrobromic acid gas; if the tube be more strongly ignited, charcoal is deposited (Löwig).—2. It burns with difficulty, but with a beautiful green flame which does not smoke, a strong odour of hydrobromic acid being at the same time evolved (Löwig).—3. It is not decomposed by nitric acid, oil of vitriol, or potassium (Löwig).—4. With ammonia, it yields hydrobromate of ethylamine:



Similarly with ethylamine, it forms hydrobromate of diethylamine; and with the latter hydrobromate of triethylamine. With phenylamine,  $NH^2.C^6H^5$ , it yields hydrobromate of ethyl-phenylamine,  $C^2H^5N.HBr$  (Hofmann).—6. With alcoholic potash-solution it forms bromide of potassium and oxide of ethyl:



(Berthelot, Ann. Ch. Pharm. xcii. 351.)

**ETHYL, CHLORIDE OF.**  $C^2H^5Cl$ . *Chlorhydric or Hydrochloric Ether, Light Muriatic Ether*. (Robiquet and Colin, Ann. Ch. Phys. [2] i. 343.—Regnault, *ibid.* lxxi. 355.—Kuhlmann, Ann. Ch. Pharm. xxxiii. 108.—Löwig, Pogg. Ann. xlv. 346.—Gm. viii. 367.—Gerh. ii. 308.)—This compound in an impure state was known to many of the older chemists, especially Rouelle; its composition was first correctly ascertained by Robiquet and Colin.

Chloride of ethyl is easily formed from alcohol and hydrochloric acid:  $C^2H^5O + HCl = C^2H^5Cl + H^2O$ ; also by distilling alcohol with various chlorides, *e.g.* chloride of aluminium, antimonie chloride, ferric chloride, pentachloride of phosphorus, dichloride of platinum, chloride of sulphur, stannic chloride, chloride of zinc, &c., its formation, especially by the action of metallic chlorides, being usually accompanied by that of oxide of ethyl (see ALCOHOL, i. 77). It is likewise produced by the action of chlorine on iodide of ethyl, by that of hydrochloric acid on acetate of ethyl, and, according to Berthelot, by heating oxide of ethyl with hydrochloric acid in sealed tubes.

*Preparation*.—1. Absolute, or at least very strong alcohol, is saturated with hydrochloric acid gas, the liquid distilled in the water-bath, and the distillate passed first into a bottle containing water, and immersed in water at  $20^\circ$ – $25^\circ C.$ , then into a receiver surrounded with ice. The product is washed either with pure or with saline water to remove free alcohol, and then rectified over magnesia.



2. Chloride of ethyl may also be prepared by distilling a mixture of 5 pts. alcohol, 5 pts. strong sulphuric acid, and 12 pts. common salt, or by distilling alcohol with the perchlorides of tin, bismuth, antimony, arsenic, or iron.

3. A convenient method of preparing chloride of ethyl in a state of purity is to act on absolute (or nearly absolute) alcohol by means of pentachloride of phosphorus. The pentachloride is contained in a flask, and, by help of a suitable arrangement, the alcohol is allowed to flow upon it in quantities of a few drops at a time, care being taken that each quantity has reacted before more is added. The mixture of hydrochloric acid gas and chloride of ethyl vapour thus formed is passed, first through a U-tube containing pieces of pentachloride of phosphorus, in order to decompose any alcohol vapour that may accompany it; then through a vessel containing water, to absorb the hydrochloric acid; next through one or two U-tubes containing fused chloride of calcium; and lastly, into a receiver cooled by a mixture of ice and salt. All the parts of the apparatus, between the generating flask and the receiver, should be kept at a temperature of 25° or 30° C., to prevent the condensation of the chloride of ethyl.

*Properties.*—Chloride of ethyl is a thin colourless liquid, of specific gravity 0.920 at 0° C. (Pierre). It boils at 11° C., and does not solidify at -29°. Its vapour-density, as determined by Thénard, is 2.219; by calculation for a condensation to 2 vol. it is 2.235 ( $\frac{2 \cdot 12 + 5 \cdot 1 + 35 \cdot 5}{2} \times 0.0693$ ). It has a pungent ethereal odour and a sweetish

aromatic taste, with somewhat alliaceous after-taste. It is very inflammable, and burns with a green-edged flame, evolving hydrochloric acid.

Chloride of ethyl dissolves sparingly in water, but mixes in all proportions with alcohol and ether. It dissolves sulphur, phosphorus, fats, volatile oils, many resins and colouring matters. It unites with several metallic chlorides.

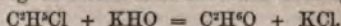
Pentachloride of antimony absorbs the vapour of chloride of ethyl, with evolution of heat, and forms a colourless liquid, which fumes in the air, and in a dry atmosphere solidifies to a crystalline mass; this, however, gradually becomes liquid and brown, and slowly deposits crystals of trichloride of antimony, whereupon water throws down a brown oil from the brown mother-liquid (Kuhlmann). Stannic chloride likewise yields, with evolution of heat, a liquid which fumes in the air, and when set aside over lime under a bell jar containing air, effloresces on the edge of the basin in plumose vegetations. Water decomposes the compound, separating part of the ether in the undecomposed state, and if the compound is not recently prepared, precipitating a white substance, probably stannic oxide (Kuhlmann). Sesquichloride of iron in dry air forms with chloride of ethyl a compound which crystallises indistinctly, and from which water throws down a large quantity of ferric oxide and separates hydrochloric ether. (Kuhlmann, Ann. Ch. Pharm. xxxiii. 108.)

Chloride of ethyl is used in medicine for the same purposes as common ether; it has been recommended in catarrhal affections. As its great volatility would interfere with its application, it is usually mixed with an equal weight of alcohol, the mixture constituting the *alcoholised muriatic ether* of the pharmacopœias.

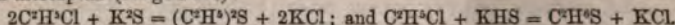
*Decompositions.* 1. By heat.—Chloride of ethyl passed through a red-hot porcelain tube is resolved into ethylene and hydrochloric acid; at a stronger heat, carbon is separated, and marsh-gas and hydrogen are obtained, as well as hydrochloric acid.—2. Cold nitric acid of specific gravity 1.3 exerts no action on chloride of ethyl; but when the vapour of that compound is passed through the boiling acid, hydrochloric acid is evolved, together with a small quantity of nitrous ether (Thénard, Boullay).—3. Sulphuric anhydride absorbs the vapour of hydrochloric ether abundantly, and converts it into a liquid, which fumes in the air, boils at 130° C., and passes over partly undecomposed, whilst the residue turns brown and gives off sulphurous acid (Kuhlmann, loc. cit.). The compound thus formed is  $\text{SO}^2 \cdot \text{C}^2\text{H}^4\text{Cl}$ , and may be regarded as chlorethylsulphuric acid  $(\text{SO}^2)^{\text{r}} \left\{ \begin{smallmatrix} \text{C}^2\text{H}^4\text{O} \\ \text{Cl} \end{smallmatrix} \right.$ , that is, as sulphuric acid

$(\text{SO}^2)^{\text{r}} \left\{ \begin{smallmatrix} \text{HO} \\ \text{HO}^{\text{r}} \end{smallmatrix} \right.$  in which 1 at. HO is replaced by peroxide of ethyl and the other by chlorine (R. Williamson, Chem. Soc. Qu. J. x. 100). Strong sulphuric acid likewise absorbs vapour of chloride of ethyl, but does not afterwards yield an oil on addition of water (Kuhlmann). It does not exert any decomposing action at medium temperatures, but when the vapour of hydrochloric ether is passed through it at a high temperature, hydrochloric acid gas is evolved (Thénard), together with ethylene gas, and ultimately also with sulphurous anhydride (Boullay).—4. In an aqueous solution of nitrate of silver, chloride of ethyl, whether in the gaseous or liquid state, forms no precipitate at first, a very slight one after an hour, and even in three months but a small quantity of chloride of silver (Thénard, Boullay); according to Thénard, it acts in a precisely similar manner on mercurous nitrate, but, according to Boullay, it immediately throws

down a large quantity of calomel from a solution of that salt. Chloride of silver is rapidly precipitated when hydrochloric ether is heated to  $100^{\circ}$  C. in a sealed tube with aqueous solution of nitrate of silver (G. C. Foster).—5. *Ammoniacal gas* and the aqueous solution of ammonia act but very slowly at ordinary temperatures on chloride of ethyl, either in the gaseous or liquid state, taking up a small quantity of chlorine from it (Thénard). A mixture of 1 vol. chloride of ethyl vapour and 2 vol. ammoniacal gas heated over the flame of a spirit-lamp, soon diminishes in volume, deposits a large quantity of sal-ammoniac, and, after being heated for some time, leaves a mixture of ammoniacal and ethylene gas (Dumas and Stas, Ann. Ch. Phys. lxxiii. 154):  $C^2H^3Cl + NH^3 = C^2H^4 + NH^4Cl$ . Chloride of ethyl acts slowly on an ethereal solution of ammonia. When the mixture is allowed to stand in stoppered bottles exposed to sunlight at the beginning of the reaction, fine crystals of hydrochlorate of ethylamine are deposited (Stas, *Kekulé's Lehrbuch*, i. 456). Chloride of ethyl, mixed with three times its volume of alcohol saturated with ammonia-gas, and heated to  $100^{\circ}$  C. for six or seven hours in a sealed tube, yields a large quantity of chloride of ethylammonium ( $N.H^3.C^2H^3$ ).Cl, together with small quantities of the chlorides of diethyl- and tetrethyl-ammonium (Groves, Chem. Soc. Qu. J. xiii. 331).—6. *Aqueous potash* at ordinary temperatures takes but a small quantity of chlorine from chloride of ethyl, even in the course of three months (Thénard). According to Boullay, the vapour of hydrochloric ether passed through a bent tube into potash-ley heated in a tubulated retort, is almost wholly decomposed, chloride of potassium being formed and alcohol having the taste and smell of rum distilling over:



A saturated alcoholic solution of potash decomposes hydrochloric ether, between  $14^{\circ}$  and  $25^{\circ}$  C., more rapidly than aqueous potash, beginning, in fact, to deposit chloride of potassium after the lapse of twenty-four hours; but the decomposition is not complete even in a week (Thénard). A mixture of alcoholic potash and hydrochloric ether inclosed in a strong glass tube and heated to  $100^{\circ}$  C. deposits chloride of potassium and forms a liquid containing common ether (Balard, Ann. Chim. Phys. [3] xii. 302). When vapour of chloride of ethyl is passed through a tube in which a mixture of lime and hydrate of potassium is gently heated, chloride of potassium is obtained, together with very pure ethylene gas (Dumas and Stas).—7. Vapour of chloride of ethyl passed into a heated alcoholic solution of *protosulphide of potassium*, is converted into sulphide of ethyl; similarly, with an alcoholic solution of sulphide of hydrogen and potassium, it forms mercaptan (Regnault):



8. *Potassium* acts rapidly on chloride of ethyl, producing an evolution of heat, whereby part of the ether is volatilised, with ebullition. If the potassium be freed by repeated pressure from the crust which forms upon it, the whole of it is ultimately converted into a white powder. This powder, when subjected to dry distillation, gives off combustible gases and leaves a carbonaceous residue, which immediately burns away on exposure to the air. It dissolves in water, with evolution of hydrogen, forming a liquid which contains a large quantity of chloride of potassium; ether shaken up with this liquid dissolves out an oil which remains behind when the ether is evaporated in vacuo, but likewise evaporates itself when left for some time in the vacuum. This oil has a peculiar odour, a soapy and somewhat burning taste, and burns with a bright flame. The white powder contains carbon and hydrogen in the proportion of 82.79 pts. to 17.21 pts.; therefore in the proportion of ethyl,  $C^2H^3$ . Hence the white powder appears to be a compound of chloride and ethylide of potassium,  $KC^2H^3$ , and the oil is perhaps a hydrate of ethyl. (Löwig, Pogg. Ann. xlv. 346.)

#### CHLORINATED DERIVATIVES OF CHLORIDE OF ETHYL.

Chlorine does not act on chloride of ethyl in the dark, and but slowly in diffused daylight; but in sunshine the action is very rapid, the liquid sometimes taking fire and depositing charcoal. If the action be set up in direct sunshine, then continued in diffused daylight, and finally completed in sunshine, the following substitution-products are formed, with evolution of hydrochloric acid:

Monochlorinated Chloride of Ethyl	.	.	$C^2H^4Cl^2 = C^2(H^4Cl^2).Cl$
Dichlorinated	"	"	$C^2H^3Cl^3 = C^2(H^3Cl^3).Cl$
Trichlorinated	"	"	$C^2H^2Cl^4 = C^2(H^2Cl^4).Cl$
Tetrachlorinated	"	"	$C^2HCl^5 = C^2(HCl^5).Cl$
Perchlorinated	"	"	$C^2Cl^6 = C^2Cl^6.Cl$

The last of these products is identical with trichloride of carbon (i. 766); the first is isomeric with dichloride of ethylene; the second, and those which follow it, with chloride of vinyl and its derivatives. (Regnault, Ann. Ch. Phys. [2] lxxi. 355.)

*Monochlorinated Chloride of Ethyl*,  $C^2H^1Cl^2 = C^2 \begin{Bmatrix} H^1 \\ Cl \end{Bmatrix}.CL$ —Isomeric with dichloride of ethylene; sometimes called *Chloraldehyde*.

The apparatus used for the preparation of this compound is similar to that which serves for the preparation of chloride of ethylene (*q. v.*). Chloride of ethyl, evolved by heating in a flask a mixture of equal volumes of alcohol and fuming hydrochloric acid, is passed through three wash-bottles, the first containing water, the second sulphuric acid, and the third water, to free it from hydrochloric acid and alcohol, and then into a glass globe, which is connected on its opposite side with another flask in which chlorine is evolved. The globe has at the bottom a narrow neck fitted into the cork of a wide-mouthed bottle, which is further connected by a bent tube with another bottle standing in a vessel of cold water, this second bottle being also provided with an escape-tube for the hydrochloric acid gas evolved. The chlorine and hydrochloric ether meeting in the glass globe are at first exposed to the rays of the sun concentrated on the vessel by a lens or mirror; but when the action has thus been set up, the vessel is placed in the shade, and the action left to go on by itself, care being taken to keep up a good stream of the vapour of chloride of ethyl, so as to prevent, as far as possible, the formation of the more highly chlorinated products. The monochlorinated hydrochloric ether thus produced, condenses, partly in the globe, partly in the wide-mouthed bottles. It is purified by shaking it up several times with water, then distilling over the water-bath, and finally rectifying over quicklime, the first drops of the distillate, which contain unaltered chloride of ethyl, being rejected, and likewise the last fourth, which generally contains the more highly chlorinated products.

Monochlorinated chloride of ethyl is a transparent, colourless, very thin liquid, of specific gravity 1.174 at 17° C. Boils at 64°. Vapour-density, by experiment 3.478, by calculation (2 vol.) 3.42. It is insoluble in water, but miscible in all proportions with alcohol and ether. Smells like Dutch liquid, and has a sweet, fiery taste. (Regnault.)

When distilled with *alcoholic potash*, it passes over for the most part unaltered; but the residue contains a small quantity of chloride of potassium, and on addition of water deposits a brown sticky resin, probably resin of aldehyde.—It may be distilled undecomposed in contact with *potassium*, the metal retaining its lustre. (Regnault.)

Monochlorinated hydrochloric ether is distinguished from Dutch liquid, which is isomeric with it, by its smaller specific gravity, lower boiling point, and difficult decomposability by potash.

*Preparation of the more highly chlorinated products.*—These are obtained by the action of chlorine on the compound just described. In diffused daylight chlorine does not exert any perceptible decomposing action on the monochlorinated chloride, but dissolves in it abundantly, imparting to the liquid an intense yellow colour. If the liquid thus saturated be exposed to sunshine, a very violent action is set up, torrents of hydrochloric acid being evolved, and the liquid often thrown out of the vessel.

On pouring a small quantity of the monochlorinated chloride into a large bottle filled with chlorine, and exposing it to sunshine, crystals of the perchlorinated compound,  $C^2Cl^4$ , are obtained after a while. The preparation of the intermediate products is somewhat difficult, but may be effected by operating as follows with a large quantity of material:

600 or 700 grammes of the monochlorinated chloride are placed in a large test-tube and covered with a layer of water. A stream of chlorine is then passed to the bottom of the tube, which is connected with a cooled receiver, and placed at first in the shade, so that the chlorine may saturate the liquid without decomposing it. The vessel is afterwards placed in a stronger light, or even in sunshine, and after the action has gone on for about two days, the liquid is distilled, and the first half of the distillate is again subjected for a while to the action of chlorine, then united with the second half, and the whole distilled in a retort fitted with a thermometer, the first and last fourths of the distillate being set aside, and the medium portion, which ought to boil at a tolerably constant temperature, being collected apart. By further fractionating this medium product into several parts, products of constant boiling point and composition will at length be obtained in a state of purity. The other fractions, which do not exhibit constant boiling points, may be used for the preparation of the more highly chlorinated products, for which purpose they are returned to the test-tube, to be again submitted to the action of chlorine, the least chlorinated being treated first.

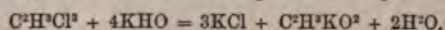
The liquid, which condenses in the cooled receiver during the action of the chlorine, is preserved for the preparation of the perchlorinated compound,  $C^2Cl^4$ .

The lower products are obtained with tolerable facility; but the preparation of those which contain the larger proportions of chlorine is much more difficult, because the quantity of liquid subjected to the action of the chlorine diminishes considerably during the operation, whereby the difficulty of separating the products by distillation



is increased. It is necessary to analyse the products from time to time, so as to make sure that the required degree of chlorination is not exceeded.

*Dichlorinated Chloride of Ethyl*,  $C^2H^3Cl^2 = C^2 \left\{ \begin{smallmatrix} H^3 \\ Cl^2 \end{smallmatrix} \right\} .Cl$ .—Isomeric with chloride of vinyl. Specific gravity 1.372 at 0° C. Boiling point 75°. Vapour-density 4.530. Its odour resembles that of Dutch liquid. It is scarcely altered by an alcoholic solution of potash, even at the boiling heat; but after the treatment has been repeated several times, chloride and acetate of potassium are produced:



It is not decomposed by alcoholic sulphhydrate of potassium.

*Trichlorinated Chloride of Ethyl*,  $C^2H^2Cl^3 = C^2 \left\{ \begin{smallmatrix} H^2 \\ Cl^3 \end{smallmatrix} \right\} .Cl$ .—Resembles the two preceding products in external characters. Specific gravity 1.530 at 17° C. Boiling point 102°. Vapour-density 5.799. Heated with alcoholic potash, it yields a certain quantity of chloride of potassium. Not attacked by sulphhydrate of potassium.

*Tetrachlorinated Chloride of Ethyl*,  $C^2HCl^4 = C^2 \left\{ \begin{smallmatrix} H \\ Cl^4 \end{smallmatrix} \right\} .Cl$ .—Difficult to obtain pure. A product not quite pure had a specific gravity of 1.644. Boiling point 146° C. Vapour-density = 6.975. It is more easily attacked than the preceding products by alcoholic potash, heat being evolved and chloride of potassium deposited; the distilled liquor diluted with water deposits an oily substance. Potassium does not act upon the tetrachlorinated compound in the cold, but on applying heat, a violent explosion takes place and carbon is deposited.

*Perchlorinated Chloride of Ethyl*,  $C^2Cl^6 = C^2Cl^5.Cl$ .—Identical with trichloride of carbon (i. 766).

*Heavy Hydrochloric Ether*, the product obtained by passing chlorine into alcohol, not long enough to convert it into chloral, and washing the product with water and potash, or by saturating alcohol with hydrochloric acid gas and distilling with peroxide of manganese, or by passing chlorine into ether and precipitating with water,—is a mixture of several products, viz. acetate of ethyl, aldehyde, chloral, chloride of ethyl, and perhaps also chloride of ethylene. (Gm. viii. 273.)

**ETHYL, CHLOROPLATINATE OF.** See ETHYLENE-CHLORIDE OF PLATINUM.

**ETHYL, CHLOROSULPHATE OF,** or *Chlorethyl-sulphuric Acid*. See p. 529; also SULPHURIC ETHERS.

**ETHYL, CYANIDE OF.**  $C^2H^3N = C^2H^3.Cy$ .—The preparation and most of the reactions of this compound are described under CYANIDES (p. 211). We have here to speak of the products of its decomposition by chlorine, as described by R. Otto. (Ann. Ch. Pharm. cxvi. 195.)

When dry chlorine gas is passed into cyanide of ethyl in a vessel exposed to diffused daylight, a large quantity of hydrochloric acid is evolved, and at the end of the reaction, which requires at last to be assisted by heat, the viscid liquid, if exposed to the temperature of a freezing mixture, deposits a crystalline substance (a), having the composition  $C^2H^4Cl^2N^2O^2$ . This substance is soluble in water, alcohol, and ether, melts at 110.5° C., and solidifies to a radio-crystalline mass at 86°. The aqueous solution is neutral, is not precipitated by nitrate of silver, and when boiled with potash gives off a large quantity of ammonia and leaves chloride of potassium.

The liquid separated from this crystalline substance (a) yields by distillation a liquid distillate (b) and a brown residue (c), which solidifies to a crystalline mass on cooling. The distillate, after repeated rectification, boils with slight decomposition at 104°—107° C., and exhibits the composition of cyanide of dichlorethyl,  $C^2H^2Cl^2N = C^2H^2Cl^2.Cy$ . Specific gravity = 1.431 at 15° C. Vapour-density, by experiment = 4.26; by calculation = 4.29. It is colourless, insoluble in water, miscible in all proportions with alcohol and ether. When kept in loosely stoppered vessels, it decomposes with abundant formation of hydrochloric acid; and when heated with potash or baryta, gives off ammonia and yields chloride of potassium or barium, together with the salt of a non-volatile acid.

The crystals which separate from the residue (c) likewise exhibit, after recrystallisation from alcohol, the composition of cyanide of dichlorethyl. They have sometimes the form of scales, sometimes that of large tables or prisms; they are colourless and inodorous, melt at 74.5° C., sublime with difficulty, and with partial decomposition, are insoluble in water, dissolve at 26° C. in 7.17 pts. of anhydrous alcohol and in 0.77 pts. ether. With alkalis they behave like the isomeric liquid compound.

**ETHYL, FLUORIDE OF.** *Hydrofluoric or Fluorhydric Ether.*  $C^2H^4F(?)$ —Produced by distilling a mixture of fluor-spar, sulphuric acid, and alcohol, or by passing dry hydrofluoric acid gas into absolute alcohol contained in a leaden or platinum vessel surrounded with ice and salt. On distilling off about one-fourth of the saturated liquid, and mixing the distillate with water, a light ethereal liquid rises to the surface, which appears to be fluoride of ethyl. It is very volatile, colourless, has a peculiar odour, like that of horse-radish, and burns with a bluish flame, giving off vapours of hydrofluoric acid. It cannot be preserved in glass vessels, at least not in contact with water, being then decomposed, with formation of alcohol and silicofluoride of potassium. It has not been obtained sufficiently pure for exact analysis. (Reinsch, J. pr. Chem. xix. 614.)

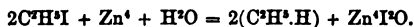
**ETHYL, HYDRATE OF.** See ALCOHOL (i. 72).

**ETHYL, HYDRIDE OF.** *Ethylide of Hydrogen.*  $C^2H^4 = C^2H^3.H$ .—This compound, which is isomeric with methyl, was originally obtained by Frankland and Kolbe in 1848 (Chem. Soc. Qu. J. i. 60) by the action of potassium on cyanide of ethyl, and was at that time regarded as methyl. Afterwards, in 1850 (Chem. Soc. Qu. J. iii. 338), Frankland obtained it by the action of water on zinc-ethyl, and showed that it is distinct from the true methyl (discovered by Kolbe in 1849), which is obtained by the electrolysis of acetic acid, and by the action of zinc on iodide of methyl.

Hydride of ethyl is produced : 1. By the resolution of a molecule of ethyl :



This decomposition takes place when iodide of ethyl is heated with zinc in a sealed tube, also when it is decomposed by light in presence of mercury (p. 525).—2. When iodide of ethyl is decomposed by zinc in presence of water or of alcohol :

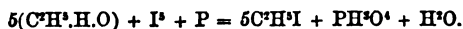


The formation of hydride of ethyl by the action of potassium on cyanide of ethyl (not quite dry), as above mentioned, was probably due to both these modes of decomposition.

**Preparation.**—When equal parts of water and iodide of ethyl are heated with zinc in a sealed and exhausted glass tube, in the manner described on page 524, decomposition takes place at a lower temperature than when zinc is heated with iodide of ethyl alone ; the decomposition is complete in about two hours. The liquid portion of the contents of the tube is thick, and solidifies on cooling to a white amorphous mass. On opening the tube under water containing sulphide of potassium, a large quantity of gas escapes, which, by combustion with oxygen, is found to have the composition of hydride of ethyl,  $C^2H^4$ .

This gas is colourless, nearly insoluble in water, but soluble in alcohol, which at  $88^\circ C$ ., and under a pressure of 665.5 mm., dissolves 1.22 of its own volume of it. (See GASES, ABSORPTION OF.) Specific gravity, by observation 1.076 ; by calculation for a condensation to 2 vol. it is 1.039. It has at first a faint ethereal smell, but becomes quite inodorous after being treated with alcohol and fuming sulphuric acid. It does not liquefy at  $-18^\circ C$ ., or even under a pressure of 20 atmospheres at  $+3^\circ$ . Chlorine does not act upon it in the dark ; but on exposing the mixture to diffused daylight, the colour of the chlorine disappears altogether. 2 vol. chlorine with 1 vol. hydride of ethyl yield 2 vol. hydrochloric acid, together with an oily liquid having the same composition per cent. as Dutch liquid. This reaction distinguishes hydride of ethyl from methyl : for when 1 vol. of the latter is mixed with 2 vol. chlorine, the products are 2 vol. hydrochloric acid and 1 vol. of a gas having the composition  $CH^4Cl$ .

**ETHYL, IODIDE OF.**  $C^2H^3I$ . *Hydriodic or Iodhydric Ether.* (Gay-Lussac [1816], Ann. Chim. xci. 89.—Serullas, Ann. Ch. Phys. [2] xxv. 323 ; xlii. 119.—E. Kopp, J. Pharm. [3] vi. 109.—R. Marchand, J. pr. Chem. xxxiii. 186.—Frankland, Chem. Soc. Qu. J. ii. 263 ; iii. 322.—Gm. viii. 359.)—This compound is produced : 1. By distilling absolute alcohol with hydriodic acid containing free iodine.—2. By the action of iodine and phosphorus on alcohol :



The phosphoric acid, at the moment of its production, acts on a sixth molecule of alcohol, in such a manner as to form ethyl-phosphoric acid,  $C^2H^3.H^3.PO^4$ .

**Preparation.**—The second reaction is almost invariably used for the preparation of iodide of ethyl. The iodine and phosphorus are either added to the alcohol in alternate small portions, or the alcohol is poured upon the whole of one of these substances,

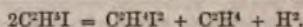


and the other is then added by small portions. Frankland pours 35 pts. absolute alcohol on 7pts. phosphorus in a vessel surrounded with ice-cold water; then adds gradually 32 pts. of iodine; decants the liquid from the undissolved portion, and distils it over the water-bath; washes the distillate, and mixes it with more iodine, till it exhibits a faint colour; then dries it over chloride of calcium; and rectifies it repeatedly over a mixture of chloride of calcium, mercury, and oxide of lead, to free it from the remaining water, and from iodine and hydriodic acid. Lautemann (Ann. Ch. Pharm. cxiii. 241) proceeds in a similar manner, pouring 10 pts. absolute or 95 per cent. alcohol on an equal weight of iodine, and very gradually adding 1 pt. of phosphorus. Hofmann (Chem. Soc. Qu. J. xiii. 69), to avoid the explosive action which takes place, even when the phosphorus is very gradually added to the mixture of iodine and alcohol, occasioning loss of material, and sometimes dangerous combustion, introduces the phosphorus, together with about one-fourth of the alcohol to be used, into a retort connected with an efficient cooler, and having inserted into its tubulus a glass globe provided with tube and stopcock. The rest of the alcohol is then poured upon the iodine, and the solution thus obtained is poured into the glass globe; the retort is heated by a sand- or water-bath till the phosphorus melts; and the alcoholic solution of iodine is then suffered to flow gradually into it. Iodide of ethyl is thus produced and distils over, together with alcohol. The rest of the iodine is then dissolved in the distillate, in which it dissolves much more freely than in pure alcohol, and the concentrated solution of iodine thus obtained is poured back into the retort, where it is immediately converted into iodide of ethyl. In preparing large quantities of iodide of ethyl by this method, it is found more advantageous to pour the whole of the alcohol at once on the phosphorus in the retort, then dissolve the iodine in previously prepared iodide of ethyl, in which it is extremely soluble, and allow this solution to flow gradually from the globe into the retort. Good proportions are 1000 grms. iodine, 700 grms. alcohol of specific gravity 0.84, and 50 grms. phosphorus. The iodide of ethyl distils over at once perfectly colourless, and requires only to be washed with water to free it from traces of alcohol. The product amounts to 96 or 98 per cent. of the theoretical quantity. It is remarkable that none of the proportions of the materials recommended for the actual preparation agree with those required by the equation above given, the theoretical quantities being about 8 pts. alcohol to 20 pts. iodine and 1 pt. phosphorus. In Hofmann's process, the quantity of phosphorus used is only  $\frac{1}{10}$  of the alcohol.

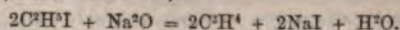
De Vrij (J. Pharm. [3] xxxi. 169) dispenses with the use of phosphorus altogether; he saturates absolute alcohol with hydrochloric acid gas in a vessel surrounded with a freezing mixture; then, having determined the proportion of hydrochloric acid in the liquid, adds this liquid to pulverised iodide of potassium contained in a tabulated retort, in quantity just sufficient to convert the whole of the iodide into chloride of potassium. The liquid containing the iodide of ethyl thus produced is distilled off next day, then washed and rectified.

*Properties.*—Iodide of ethyl is a colourless liquid, having a strong, peculiar ethereal odour. Specific gravity 1.9206 at 23° C. (Gay-Lussac), 1.97546 at 0° (Pierre), 1.9464 at 16° (Frankland). It boils at 70° (Pierre), with the barometer at 751 mm.; at 72.2° (Frankland), barometer at 746.5 mm. Vapour-density, by experiment = 5.475 (Gay-Lussac), by calculation (2 vol.) = 5.405. It is but slightly soluble in water, but mixes readily with alcohol and ether.

*Decomposition.*—1. Iodide of ethyl is but slightly inflammable; when dropped on red-hot coals, it gives off violet vapours without taking fire.—2. When its vapour is passed through a porcelain tube heated to dull redness, hydrogen, ethylene, and iodide of ethylene are obtained, and sometimes iodine is set free (E. Kopp):



3. When exposed to *light*, it turns red or brown, from separation of the iodine and ethyl, the decomposition taking place slowly in diffused daylight, quickly in sunshine. If the iodine be removed by mercury, the compound is at length completely decomposed, yielding, in sunshine, ethyl and iodide of mercury, the former being partly resolved into ethylene and hydride of ethyl. In diffused light, the chief product of the decomposition is iodide of mercuriethyl,  $C^2H^5Hg^2I$ .—4. *Chlorine* converts iodide of ethyl into chloride, separating the iodine if the action is rapid, but forming chloride of iodine if it is slower.—5. Strong *nitric acid* also separates iodine from iodide of ethyl. Strong *sulphuric acid* blackens it.—6. Aqueous *potash* acts upon it but slowly.—7. When the vapour is passed over hot *soda-lime*, pure ethylene is set free, and iodide of sodium is formed (Dumas and Stas):



8. *Metals* decompose iodide of ethyl under the influence of light or heat, with various



degrees of facility; generally speaking, the metal unites, partly with the iodine, partly with the ethyl; sometimes, however, the organo-metallic compound thus formed acts further on the metallic iodide, or on the undecomposed iodide of ethyl, giving rise to new products.

The reactions with zinc and zinc-ethyl have been already described (pp. 524, 532), *Sodium-ethyl* acts in the same manner as zinc-ethyl, without the aid of heat, evolving a pure mixture of ethylene and hydride of ethyl (Frankland):



Iodide of ethyl enclosed in a sealed tube, with thin strips of *tin-foil*, and heated to 180° C., or exposed to the sun's rays concentrated by a lens or mirror, is partly decomposed, yielding ethyl and iodide of tin, while the rest unites with the metal, forming iodide of stannethyl  $(\text{C}^2\text{H}^3)_2\text{Sn}^2\text{I}^2$  (Frankland, Chem. Soc. Qu. J. vi. 57). According to Cahours (Ann. Ch. Phys. [3] lviii. 5), iodide of tristannethyl,  $\text{Sn}^2(\text{C}^2\text{H}^3)_3$ , is formed at the same time. When an alloy of tin and sodium is used, several other stannides of ethyl are likewise produced (Löwig, J. pr. Chem. lxxv. 386; Jahresber. d. Chem. 1862, p. 577). *Arsenide of sodium* or of *potassium*, heated with iodide of ethyl, yields the compounds  $\text{As}(\text{C}^2\text{H}^3)_3$ ,  $\text{As}(\text{C}^2\text{H}^3)_2$ , and  $\text{As}(\text{C}^2\text{H}^3)\text{I}$ ; *antimony* or *antimonide of sodium* yields stibtriethyl  $\text{Sb}(\text{C}^2\text{H}^3)_3$ . *Arsenide of zinc* or *arsenide of cadmium*, heated with iodide of ethyl in sealed tubes, yields a compound of iodide of zinc or cadmium with iodide of tetrethylarsonium,  $\text{As}(\text{C}^2\text{H}^3)_4\text{I} \cdot \text{ZnI}$  or  $\text{As}(\text{C}^2\text{H}^3)_4\text{I} \cdot \text{CdI}$ . *Phosphide of zinc* yields a similar compound, containing phosphorus in place of arsenic. *Plumbide of sodium* yields  $\text{Pb}(\text{C}^2\text{H}^3)_2$ , together with several other compounds (Löwig); *bismuthide of sodium* forms  $\text{Bi}(\text{C}^2\text{H}^3)_3$ .

*Aluminium*, heated with iodide of ethyl, yields a fuming liquid, which boils at 340°–350° C., and exhibits the composition  $\text{Al}^3(\text{C}^2\text{H}^3)_3\text{I}^3$  or  $\text{Al}^2\text{I}^3 \cdot \text{Al}^3(\text{C}^2\text{H}^3)_3$ . This iodide decomposes explosively in contact with water, forming alumina, hydriodic acid, and hydride of ethyl; in an atmosphere of chlorine or oxygen it takes fire. Zinc-ethyl acts strongly on it, producing iodide of zinc, and a very inflammable liquid, which has not been obtained pure, but appears to have the composition of aluminium-ethyl.  $\text{Al}^3(\text{C}^2\text{H}^3)_3$ . (Cahours.)

Similar results have been obtained by Hallwachs and Schafarik (Ann. Ch. Pharm. cxix. 206).

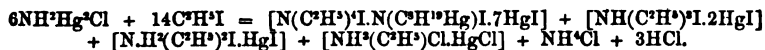
*Glucinum* reacts with iodide of ethyl like aluminium, and appears to form similar products. (Cahours.)

*Magnesium*, in the form of filings, acts spontaneously and with rise of temperature on iodide of ethyl. If the tube, after cooling, be sealed, and then heated for some hours to 120°–130° C., a white mass is formed which, when distilled, yields magnesium-ethyl mixed with iodide of ethyl. The magnesium-ethyl, separated by fractional distillation, is a colourless, alliacious, spontaneously inflammable liquid, which decomposes water with violence. (Cahours, loc. cit.; see also Hallwachs and Schafarik, loc. cit.)

Pulverised *vanadium* acts slowly on iodide of ethyl at 180° C., forming a deep red liquid. (Hallwachs and Schafarik.)

The action of *mercury* on iodide of ethyl has been already described (pp. 524, 525).

9. When pulverised *white precipitate*  $(\text{NH}^+\text{Hg}^+)\text{Cl}$ , triturated with water, is heated with iodide of ethyl for several days at the temperature of the water-bath, no gas is evolved, but gold-yellow crystals are formed, consisting of a compound of mercuric iodide with iodide of tetrethylammonium and iodide of mercurotetrethylammonium; these crystals are surrounded by a dark brown liquid containing compounds of mercuric iodide with the iodides of ethylammonium, diethylammonium, and triethylammonium, and on this there floats a nearly colourless aqueous solution containing mercuric chloride, sal-ammoniac, and a crystallisable compound of mercuric chloride and chloride of ethylammonium:



(Sonnenschein, Ann. Ch. Pharm. ci. 20.)

10. Iodide of ethyl dissolved in alcohol is decomposed by most *silver-salts*, in the same manner as the iodides of the alkali-metals, iodide of silver being precipitated, and the solution containing the ethyl-salt of the acid previously united with the silver. A similar decomposition takes place, and with greater facility, when a silver-salt is heated with dry iodide of ethyl in a sealed tube. This is a very convenient way of preparing many compound ethers: thus *orthophosphate*, *pyrophosphate*, *sulphate*, *sulphide*, *cyanide*, and *sulphocyanate of silver*, heated in sealed tubes with iodide of ethyl, yield the corresponding ethyl-ethers. According to Gössmann (Ann. Ch. Pharm. ci. 218) *tungstate of silver* and iodide of ethyl, enclosed together in a sealed tube, act upon

each other strongly at ordinary temperatures, evolving great heat, forming iodide of silver and oxide of ethyl, and liberating tungstic anhydride. According to H. B. Nason (Ann. Ch. Pharm. civ. 126) iodide of ethyl acts in a precisely similar manner, but with various degrees of facility, on *molybdate*, *arsenite*, *arsenate*, *antimonate*, *stannate*, *borate*, and *tellurate* of silver. With neutral or acid *chromate* of silver, it yields a small quantity of aldehyde.

The *cyanides of potassium and barium*, heated with iodide of ethyl in sealed tubes, yield an iodide of the metal and cyanide of ethyl; *cyanide of zinc* does not appear to act upon it at 140°–160° C. *Cyanide of mercury* and iodide of ethyl decompose each other to a slight extent, even when their alcoholic solutions are simply mixed and evaporated; in sealed tubes at 120° C. the decomposition is more complete. The *metallic sulphocyanates*, heated with iodide of ethyl in sealed tubes to 100°–160°, yield sulphocyanate of ethyl; *sulphocyanate of mercury* produces a more complicated reaction, the products of which have not been examined. The *acetates of potassium, barium, lead, mercury, and silver*, heated to 200° C. with iodide of ethyl in sealed tubes, yield metallic iodide and acetate of ethyl. With the *formates*, the decomposition is less easy; but it is facilitated by the presence of a certain quantity of alcohol. The *oxalates* are decomposed in like manner, but the resulting oxalate of ethyl is decomposed at the high temperature of the reaction, yielding carbonic oxide and carbonic anhydride, which burst the tubes when they are opened, with a loud detonation. (Schlagdenhauffen, Ann. Ch. Pharm. cvii. 234; ex. 256.)

11. A mixture of 2 pts. iodide of ethyl and 1 pt. *disulphide of carbon*, shaken up in a corked flask with *sodium-amalgam*, yields, as principal product, a fetid liquid having the composition of trisulphide of allyl ( $C^3H^3S^3$ ). This liquid has a specific gravity of 1.012 at 15° C.; boils at 188° C.; is insoluble in water; mixes in all proportions with alcohol, ether, and disulphide of carbon; is decomposed with violence by fuming nitric acid, chlorine, bromine, and hypochlorite of calcium; is not decomposed by sodium, potash, alkaline sulphides, or mercuric oxide, but yields with alcoholic mercuric chloride, a white precipitate having the composition  $12HgCl.(C^3H^3S^3)_2$ .

12. Iodide of ethyl, heated with *alcoholic ammonia* in such a manner that the volatilised portions may condense and run back again, yields a mixture of the iodides of ammonium, and of ethyl-, diethyl-, triethyl-, and tetrethyl-ammonium (Weltzien, Ann. Ch. Pharm. lxxvi. 202). With *triethylamine* it solidifies to a crystalline mass of iodide of tetrethylammonium; and with triamines in general it forms the iodide of an ammonium containing ethyl, in addition to the radicals of the triamine. (Hofmann.)

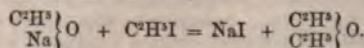
#### ETHYL, NITRIDES OF. See ETHYLAMINES.

**ETHYL, OXIDE OF.**  $C^2H^3O = \begin{smallmatrix} C^2H^3 \\ C^2H^3 \end{smallmatrix} O$ . Ether, *Ethylic ether*, *Vinic ether*;

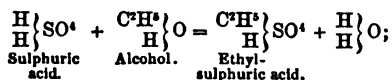
formerly called *Sulphuric ether*, *Phosphoric ether*, &c., according to the acid used in its preparation. (Gm. viii. 17.—Gerh. ii. 270.—Kekulé, *Lehrb. der org. Chemie*, p. 100.)

Valerius Cordius, in 1540, first described the preparation of ether, which he called *Oleum vitrioli dulce*. Frobenius, who first called it *ether*, again directed attention to it in 1730. Afterwards the ether prepared by the action of sulphuric acid upon alcohol was called *sulphuric ether*; but Valentin Rose (Scher. J. iv. 263) showed that it does not contain sulphur. Fourcroy suggested that ether is alcohol deprived of a certain portion of oxygen and hydrogen; a suggestion which was confirmed, so far as regards the percentage composition, by the analyses made by Saussure and by Dumas and Boullay (Ann. Ch. Phys. xxxvi. 294).—Boullay discovered the preparation of ether by phosphoric acid (Ann. Chim. lxii. 192), and by arsenic acid (*ibid.* lxxviii. 284); he likewise first practised the preparation of ether by the continuous process (J. Pharm. i. 97).—Desfosses prepared it with fluoride of boron (Ann. Ch. Phys. [2] xvi. 72); Masson with chloride of zinc; Kuhlmann with tetrachloride of tin, and other metallic chlorides. The constitution of ether was further studied by Liebig (Ann. Ch. Pharm. ix. 1; xxx. 138).—Malaguti (Ann. Ch. Phys. [2] lxx. 338; [3] xvi. 5), and Regnault (*ibid.* [2] lxxi. 352), investigated the products of its decomposition by chlorine. Graham in 1850 (Chem. Soc. Qu. J. iii. 24) made some important experiments on the formation of ether by the action of acids and salts on alcohol under pressure; and Williamson in the same and the following year (Phil. Mag. [3] xxxvii. 350; Chem. Soc. Qu. J. iv. 106) established the views of the constitution and formation of ether now universally adopted. Lastly, Reynoso in 1856 published an elaborate series of investigations on the etherification of alcohol by acids, salts, &c. (Ann. Ch. Phys. [3] xlviii. 385.)

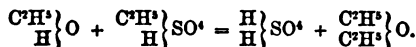
**Formation.**—1. By the action of iodide (bromide or chloride) of ethyl on ethylate of potassium or sodium. (Williamson.)



2. By heating a mixture of alcohol and strong sulphuric acid to a temperature between  $140^{\circ}$  and  $150^{\circ}$  C. (about  $280^{\circ}$  to  $300^{\circ}$  F.). The formation of ether here takes place by two stages; the first consisting in the formation of ethylsulphuric acid and water:



the second in the production of ether, and reproduction of sulphuric acid, by the mutual action of ethylsulphuric acid and another molecule of alcohol:



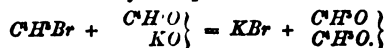
The sulphuric acid being thus reproduced in its original state, is ready to etherify fresh quantities of alcohol, so that, if the supply of alcohol is made continuous, the process goes on without interruption. The water formed in the first stage of the reaction does not, however, distil over quite so fast as it is formed, and consequently the sulphuric acid becomes continually more dilute, and at last too weak to etherify the alcohol.

The action of phosphoric and of arsenic acid is similar to that of sulphuric acid.

The formation of ether by the action of these and other dehydrating substances was formerly attributed to the simple abstraction of water, ether being represented by the formula  $\text{C}^2\text{H}^5\text{O}$ , and alcohol by  $\text{C}^2\text{H}^5\text{O}^2$  or  $\text{C}^2\text{H}^5\text{O}.\text{HO}$ ; but the manner in which the reaction takes place, and its relation to other reactions in which ethylic ether or analogous products are formed, clearly show that this is not the right view of it. In the *first* place, during the whole of the distillation, ether and water go off together, the quantity of water thus evolved being nearly equal to the whole of that which, according to the old view of the reaction, should be separated from the alcohol and taken up by the sulphuric acid. *Secondly*, ethyl-sulphuric acid is always formed on heating together alcohol and sulphuric acid; and ethyl-sulphuric acid, heated with alcohol, does actually give off ether. *Thirdly*, if, in the first mode of formation, the ethylate of potassium be mixed with iodide of methyl or amyl instead of iodide of ethyl, the product is an intermediate ether,  $\begin{array}{c} \text{C}^2\text{H}^5 \\ \text{C}^2\text{H}^5 \end{array} \left\{ \text{O} \right.$  or  $\begin{array}{c} \text{C}^2\text{H}^5 \\ \text{C}^2\text{H}^{11} \end{array} \left\{ \text{O} \right.$ ; or if, in the second, a stream of ethylic alcohol be made to flow into a heated mixture of sulphuric acid and amylic alcohol, ethyl-amylic ether,  $\begin{array}{c} \text{C}^2\text{H}^5 \\ \text{C}^2\text{H}^{11} \end{array} \left\{ \text{O} \right.$ , distils over, and ethyl-sulphuric acid remains in the vessel. These reactions are precisely analogous to those by which oxide of ethyl is produced, and show that this compound differs from the double ethers,  $\begin{array}{c} \text{C}^2\text{H}^5 \\ \text{C}^2\text{H}^{11} \end{array} \left\{ \text{O} \right.$ , for example, only in containing 2 at. ethyl instead of 1 at. ethyl and 1 at. amyl. *Fourthly*, the vapour-densities of alcohol and ether show that a given volume of ether in the state of vapour contains twice as much ethyl as the same volume of alcohol-vapour, and therefore, according to the general law of vapour-volumes, the molecule of ether must be  $(\text{C}^2\text{H}^5)^2\text{O}$ , if that of alcohol is  $\text{C}^2\text{H}^5.\text{H}.\text{O}$ . *Fifthly*, if the simple and double ethers are represented by corresponding (2-volume) formulæ, their formulæ constitute an ascending series, corresponding very nearly with their differences of boiling point; thus:

				Boiling point.
Methylic ether	$\text{C}^2\text{H}^4\text{O} =$	$\text{CH}^3.\text{CH}^3.\text{O}$	.	— $21^{\circ}$ C.
Methyl-ethylic ether	$\text{C}^2\text{H}^6\text{O} =$	$\text{CH}^3.\text{C}^2\text{H}^5.\text{O}$	.	+ 11
Ethylic ether	$\text{C}^4\text{H}^{10}\text{O} =$	$\text{C}^2\text{H}^5.\text{C}^2\text{H}^5.\text{O}$	.	+ 34
Methyl-amylic ether	$\text{C}^4\text{H}^{14}\text{O} =$	$\text{CH}^3.\text{C}^2\text{H}^{11}.\text{O}$	.	+ 92
Ethyl-tetrylic ether	$\text{C}^4\text{H}^{14}\text{O} =$	$\text{C}^2\text{H}^5.\text{C}^2\text{H}^9.\text{O}$	.	+ 80
Ethyl-amylic ether	$\text{C}^6\text{H}^{18}\text{O} =$	$\text{C}^2\text{H}^5.\text{C}^2\text{H}^{11}.\text{O}$	.	+ 112
Tetrylic ether	$\text{C}^6\text{H}^{18}\text{O} =$	$\text{C}^2\text{H}^9.\text{C}^2\text{H}^9.\text{O}$	.	+ 104
Amylic ether	$\text{C}^{10}\text{H}^{22}\text{O} =$	$\text{C}^2\text{H}^{11}.\text{C}^2\text{H}^{11}.\text{O}$	.	+ 176

If the simple ethers are represented by one-volume formulæ, and the double ethers by two-volume formulæ, this gradation no longer exists. *Sixthly*, when bromide of ethyl is heated with an alcoholic solution of potash, the products formed are bromide of potassium and ether. Now, if the ether were  $\text{C}^2\text{H}^5\text{O}$ , the reaction must take place according to the equation:  $\text{C}^2\text{H}^5\text{Br} + \text{KO} = \text{C}^2\text{H}^5\text{O} + \text{KBr}$ , the alcohol acting merely as a solvent; whereas if ether is  $(\text{C}^2\text{H}^5)^2\text{O}$  or  $(\text{C}^2\text{H}^5)^2\text{O}$ , the alcohol must take part in the reaction, in the manner shown by the equation:

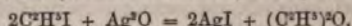




Now Berthelot found (Ann. Ch. Pharm. xcii. 131) that 22 grms. of bromide of ethyl thus treated yielded 12 grms. of ether, the theoretical quantity being 7.6 according to the first supposition, and 15 according to the second. Hence, allowing for unavoidable loss in rectifying the product, the result may be taken as a proof that the alcohol reacts in the manner shown by the second of the above equations, and that the molecule of ether contains 2 at. ethyl. (See the articles ALCOHOL, i. 76; and CHEMICAL AFFINITY, i. 867.)

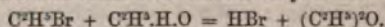
Ether is also produced by the following reactions:—

3. By the action of iodide (bromide or chloride) of ethyl on dry oxide of silver:

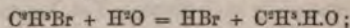


Other ethyl-salts—the nitrate for example—act in a similar manner.

4. By heating alcohol with bromide or iodide of ethyl to 200° C. (Reynoso.)



5. By heating bromide or iodide of ethyl with water to 150°–200° C. (Frankland, Reynoso). In this case, alcohol is first formed, according to the equation:



and this alcohol, acting on the excess of iodide or bromide of ethyl, forms ether, as in 4.

6. By heating alcohol to 200°–240° C. with hydrochloric, hydrobromic, or hydriodic acid. Chloride, bromide, or iodide of ethyl is then formed, which acts upon the remaining alcohol as in 4, converting it into ether.

7. The same action is exerted by metallic chlorides, when distilled with alcohol, or better, when heated with it in sealed tubes, *e. g.* by chloride of zinc, tetrachloride of tin, the chlorides of manganese, cobalt, nickel, and cadmium, ferrous chloride, mercuric chloride, &c. (Reynoso.) Even chloride of calcium and chloride of strontium convert alcohol into ether, when heated with it to 300° C. (Berthelot, Ann. Ch. Pharm. lxxxiii. 104.)

The etherifying actions of iodide of mercury (Reynoso), of fluoride of boron, and of fluoride of silicium, belong to the same category.

8. Many sulphates also convert alcohol into ether when heated with it to 200°–230° C., ethylsulphuric acid being first formed, and then producing ether with the rest of the alcohol; etherification is thus effected by the sulphates of magnesium, zinc, and cadmium, by ferrous, cobaltous, and uranic sulphate, also by sulphate of aluminium, common alum, ammonia-, iron-, and chrome-alum. (Reynoso.)

*Preparation.*—Ether is always prepared by heating a mixture of alcohol and sulphuric acid. The best mode of conducting the operation is that introduced by Boullay, in which the alcohol is supplied in a constant stream and the formation of ether goes on uninterruptedly (p. 537). A mixture of 5 pts. alcohol of 90%, and 9 pts. strong sulphuric acid is introduced, after cooling, into a wide-mouthed flask closed with a cork having three apertures, through one of which there passes a bent tube proceeding from a reservoir of alcohol, and terminating in a narrow mouth below the surface of the liquid in the flask; the reservoir is provided with a stop-cock to regulate the flow of spirit. Through the second aperture is inserted another bent tube, terminating just below the cork, and passing to a Liebig's condenser or a worm-tub connected with a receiver. The third aperture is for the insertion of a thermometer. The flask is heated in a sand-bath, and as soon as it begins to boil, the alcohol from the reservoir is allowed to flow in, the stream being regulated so as to keep the temperature of the liquid at about 140° C. (284° F.); below this temperature, the distillate consists chiefly of alcohol, and at higher temperatures large quantities of olefant gas are evolved. The process may be continued till the quantity of alcohol run in amounts to about six times that which was originally mixed with the sulphuric acid, making in all 35 pts. alcohol to 9 pts. acid. After this the sulphuric acid becomes too dilute to etherify the alcohol effectually. The alcohol which remains mixed with the sulphuric acid at the end of the process, may be recovered by mixing the liquid with water and distilling. On the large scale, a still of cast-iron lined with lead is generally used; it has, however, the disadvantage of not allowing the course of the operation to be watched. To moderate the great heat evolved on mixing large quantities of alcohol and sulphuric acid, the mixture is made in a metallic vessel surrounded with cold water or ice, and the sulphuric acid is poured down the side, so that it may form a layer below the alcohol. The two liquids are then slowly mixed by stirring with a wooden spatula, and the mixture when sufficiently cool, is transferred to the still. The distillation is conducted in the manner above described.

The first portions of the distillate separate spontaneously into two layers, the upper consisting of ether, mixed with comparatively small quantities of alcohol and water,

the lower of water, containing ether and alcohol in solution; but towards the latter part of the distillation, when the sulphuric acid has become weaker, more alcohol passes over unchanged, and the separation of the ether no longer takes place. The distillate also contains sulphurous acid, acetic acid, and a little oil of wine. To purify it, the whole of the distillate is introduced, together with an equal volume of milk of lime, into a large separating globe, having a descending tube and stopcock like a tap-funnel; the mixture is frequently agitated, and then left to itself till the ether has risen to the top, after which the lime-solution is run off by the stopcock, and the ether which remains is rectified over a water-bath. Nearly pure ether, amounting to one-third of the crude ether in the retort, then passes over first; afterwards ether containing alcohol; then alcohol containing oil of wine; and lastly water.

The rectified ether still retains a little water and alcohol; but it is pure enough for most purposes; it should, however, be quite free from sulphurous acid, and therefore should not redden litmus paper. 100 pts. alcohol containing 85 pts. by weight of absolute alcohol (after deducting that which remains in the flask) yield, in a well conducted process, 69 or 80 pts. by weight of ether, of specific gravity 6.725, or 70% of the (absolute) alcohol used. If the whole of the alcohol were converted into ether, the yield would be 80 per cent.

Soubeiran (J. Pharm. [3] xvi. 321) describes an apparatus for the preparation of ether on the large scale, by which the ether is at once obtained in the rectified state, the first condensing vessels being kept (as in the more recently invented apparatus for the distillation of brandy) at a sufficiently high temperature to maintain the pure ether in the state of vapour. He recommends that the temperature of the etherifying mixture be kept constantly at 130° C., because at 140° a gaseous hydrocarbon is constantly produced. An apparatus for the rectification of ether has also been described by Hoyer (Arch. Pharm. [2] xiii. 140).

The ordinary ether, obtained as above, may be completely freed from water and alcohol, and converted into absolute ether, either by placing it in contact with lumps of fused chloride of calcium, which takes up the water and alcohol, and separates from the ether in the form of a thick heavy liquid, or by agitating it repeatedly with 2 pts. of water, separating the upper layer of liquid by a pipette or tap-funnel, then leaving it for some time in contact with quick-lime or chloride of calcium, and rectifying.

Absolute ether should form a clear mixture in all proportions with oil of copaiba; ether containing water or alcohol forms an emulsion with considerable quantities of the oil. (Blanchet, Ann. Ch. Pharm. vii. 157.)

*Properties.*—Pure ether is a colourless, transparent, very mobile liquid, having a peculiar exhilarating odour and sharp, burning taste, with cooling after-taste. It is perfectly neutral to vegetable colours; refracts light strongly. Specific gravity 0.723 at 12.5° C. Boiling point 35.6° C. (96° F.) under a pressure of 760 mm. Vapour-density 2.586 (Gay-Lussac); by calculation for the formula (C<sup>2</sup>H<sup>5</sup>)<sub>2</sub>O, representing a condensation to 2 volumes, it is 2.564 (=  $\frac{4 \cdot 12 + 10 \cdot 1 + 16}{2} \times 0.0693$ ). Cooled

to - 31° C. it crystallises in white shining laminae. It is very inflammable, and its vapour, when mixed with air, detonates with great violence on the approach of a burning body. As the vapour of ether has a considerable tension at ordinary temperatures, and consequently diffuses quickly to a considerable distance, great danger is incurred in pouring the liquid from one vessel to another, in the neighbourhood of a gas-light or any burning body. The decantation of any considerable quantity of ether should always be performed in a room where there are no lights burning.

Ether mixes in all proportions with *alcohol*, *wood-spirit*, *chloroform*, *acetone*, and many other liquids, and to a certain extent also with *water*. When ether is shaken up with water, two layers are formed, the upper consisting of ether containing a little water, and the lower of water which has dissolved  $\frac{1}{10}$  of ether. Ether dissolves *iodine* and *bromine*, and small quantities of *sulphur* and *phosphorus*; also *chloride of gold*, *chloride of iron*, *mercuric chloride*, and *mercuric nitrate*. It dissolves with facility most organic bodies containing a large proportion of hydrogen, such as *fats* and *resins*, which are but sparingly dissolved by alcohol, whereas it acts but little on those which are easily soluble in alcohol.

Ether unites directly with *tetrachloride of tin*, forming the compound 2C<sup>2</sup>H<sup>5</sup>O.SnCl<sub>4</sub>, which crystallises in shining rhomboidal plates, volatile without decomposition, dissolving easily in excess of ether, and decomposing in contact with water.

*Decompositions.*—1. By *Heat*. Ether-vapour, passed through a red-hot tube, yields nearly the same products as alcohol, viz. olefiant gas, carbonic oxide, water, aldehyde, &c.—2. By *Combustion*. When ether burns rapidly in the air or in oxygen gas, it is completely converted into water and carbonic anhydride; but when ether-vapour mixed with air comes in contact with platinum-black, slightly heated platinum-sponge,

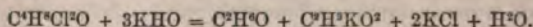


or other bodies heated not quite to redness, it undergoes a slow and imperfect combustion, like alcohol under similar circumstances, yielding various products of oxidation, viz. aldehyde, acetic acid, formic acid, carbonic acid, water, and a peculiar volatile, pungent substance, which has been called *acetyloous, aldehydic, or lampic acid*, but has not been isolated: it is probably only a mixture of the products just mentioned (see ACETYLEOUS ACID, i. 36; ALCOHOL, i. 74; COMBUSTION, i. 1093). Ether exposed to the air in contact with potash yields a small quantity of acetate of potassium.—3. Ether mixed with strong *sulphuric acid* and heated to 120° C. does not give off any gas, and if water be then added, a solution is formed containing nothing but ethyl-sulphuric acid. If, on the other hand, the heat be raised above 120° C. the liquid begins to boil at 130°, and at 150° gives off sulphurous anhydride; at 180° it is in full ebullition, gives off oil of wine impregnated with sulphurous acid, and blackens considerably; the residue contains isethionic and ethionic acids.—4. Ether is decomposed by heated *nitric acid*, yielding carbonic anhydride, acetic acid, and oxalic acid.—5. *Chloric* and *bromic acids* likewise oxidise it rapidly, acetic acid being formed, and chlorine or bromine evolved.—6. With *hydrochloric acid* gas it forms chloride of ethyl.—7. Dry *chlorine* passed into anhydrous ether, forms three substitution products,  $C^2H^4Cl^2O$ ,  $C^2H^4Cl^1O$ , and  $C^2H^4Cl^0O$ , besides aldehyde, chloral, chloride of ethyl, and hydrochloric acid. If water is present, acetic acid and other products of oxidation are formed.—8. *Bromine* appears to act upon ether like chlorine. The red solution of bromine in ether becomes colourless after a few days, with formation of hydrobromic acid, bromide of ethyl, bromal, and other products, forming together a mixture analogous to heavy hydrochloric ether (p. 532). With *chloride of bromine*, ether yields hydrochloric acid and an organic compound rich in bromine.—9. *Iodine* acts but slightly upon ether. *Chloride of iodine* forms hydrochloric acid, the iodine dissolving in the ether.—10. *Phosphorus* converts ether into several phosphorised acids, which have not been accurately studied.—11. *Potassium* and *sodium* slowly decompose ether, eliminating hydrogen (Thénard.) [Was the ether quite free from water and alcohol?].—12. When ether-vapour is passed over heated *potash-* or *soda-lime*, hydrogen and marsh-gas are given off, and an alkaline carbonate is formed.—13. Ether decomposes many *metallic chlorides*, abstracting the chlorine, and yielding products which are probably the same as those produced by the action of free chlorine on ether. *Sesquichloride of iron* is decolorised and reduced to protochloride, with formation of hydrochloric acid; *cupric chloride* to cuprous chloride; *mercuric chloride* to mercurous chloride, which is precipitated; from *chloride of gold*, in sunshine, metallic gold is deposited.

#### CHLORINATED AND SULPHURETTED DERIVATIVES OF ETHYLIC ETHER.

Anhydrous ether treated with chlorine yields three substitution-products, containing 1, 2, and 4 at. chlorine in place of hydrogen, according to the manner and duration of the action. These compounds have been investigated chiefly by Regnault (Ann. Ch. Phys. [2] lxxi. 392), Malaguti (*ibid.* [2] lxx. 338; [3] xvi. 5 and 19), and Lieben (Ann. Ch. Pharm. cxi. 121).

*Monochlorethylic Ether*,  $C^2H^4Cl^1O = \begin{matrix} C^2H^4Cl \\ C^2H^4Cl \end{matrix} O$ .—This compound, originally called *chlorethetal*, was discovered in 1837 by D'Arcet (Ann. Ch. Pharm. xxviii. 82), who obtained it by the action of chlorine on olefiant gas. Regnault, however, suggested that its production was due to the presence of ether-vapour in the gas; and Lieben has since shown that the same compound is the chief product of the action of chlorine on ether at temperatures not exceeding 20°–30° C. It is a very mobile, limpid, colourless liquid, having a sweet, ethereal odour, and boiling between 140° and 147°. Vapour-density = 4.93. Water decomposes it, yielding a substance which appears to be isomeric with aldehyde or acetate of ethyl. With potash it yields alcohol and acetic acid:



*Dichlorethylic Ether*,  $C^2H^4Cl^2O = \begin{matrix} C^2H^4Cl^1 \\ C^2H^4Cl^1 \end{matrix} O$ .—Discovered by Malaguti in 1839. Produced when pure ether is saturated with chlorine in diffused daylight, the liquid being cooled at first, and afterwards heated to 100° C. A large quantity of hydrochloric acid is formed in the reaction, together with chloride of ethyl and chloral; the hydrochloric acid, acting on the ether, forms chloride of ethyl and water, and the chlorine, in presence of the water, exerts an oxidising action, resulting in the formation of chloral.

Dichlorethylic ether is a limpid liquid, of specific gravity 1.5008, having an odour like that of fennel. It is decomposed by heat, even below its boiling point, with evo-



lution of hydrochloric acid. It is slowly decomposed by water and by aqueous potash, quickly by alcoholic potash, yielding chloride and acetate of potassium:



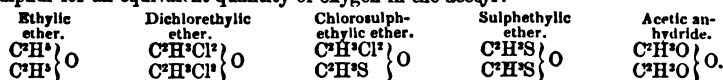
Potassium decomposes it at a gentle heat, forming a chloride of potassium, and eliminating a gas, which burns with a green flame. Chlorine, in sunshine, converts dichlorethylic into perchlorethylic ether.

Sulphydric acid decomposes dichlorethylic ether, with evolution of hydrochloric acid and formation of an oily liquid, which solidifies in a few days to a soft crystalline mass, separable by crystallisation from boiling alcohol into the two following compounds containing respectively 1 and 2 at. sulphur in place of 2 and 4 at. chlorine:

*Sulphethylic Ether*,  $\text{C}^2\text{H}^2\text{S}^2\text{O}$  (Malaguti's *ether sulfuré*), crystallises out first in prismatic needles, having a faint odour like that of chloride of sulphur, melting between  $120^\circ$  and  $123^\circ$  C., insoluble in water, but soluble in alcohol and ether; decomposed by alcoholic potash, yielding sulphide and acetate of potassium.

*Chlorosulphethylic Ether*,  $\text{C}^2\text{H}^2\text{Cl}^2\text{SO}$  (Malaguti's *ether chlorosulfuré*), crystallises from the mother-liquor of the preceding, in unctuous fetid scales, melting between  $70^\circ$  and  $72^\circ$  C., insoluble in water, soluble in alcohol and ether. Alcoholic potash converts it into sulphide, chloride, and acetate of potassium.

These sulphuretted compounds, as well as the dichlorinated ether from which they are formed, may be regarded as intermediate in composition between ethylic ether and acetic anhydride, and as derived from the latter by the substitution of chlorine or sulphur for an equivalent quantity of oxygen in the acetyl:



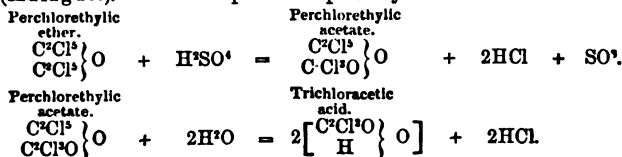
All these compounds, when treated with potash, yield acetate of potassium.

*Perchlorethylic Ether*,  $\text{C}^2\text{Cl}^4\text{O} = \left. \begin{array}{c} \text{C}^2\text{Cl}^3 \\ \text{C}^2\text{Cl}^3 \end{array} \right\} \text{O}$ .—Discovered by Regnault in 1830.

Produced by the prolonged action of chlorine on ether, in sunshine. In preparing this and the other chlorinated derivatives of ether, it is advisable not to cool the liquid too much at the beginning, so as to allow the hydrochloric ether, which is produced in large quantity, to escape; otherwise the reaction is apt to become very complicated, and to yield especially large quantities of perchlorinated chloride of ethyl or trichloride of carbon (p. 532).

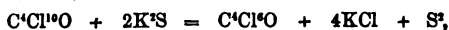
Perchlorethylic ether crystallises in dimetric octahedrons, differing but little from regular octahedrons. Length of principal axis = 0.952. P : P in the lateral edges =  $106^\circ 46'$ . Terminal summits truncated by the face oP. Cleavage parallel to oP (Nicklès, Ann. Ch. Phys. [3] xxii. 28). Specific gravity = 1.9 at  $14.5^\circ$  C. (Malaguti). Melts at  $69^\circ$  C. (Regnault), and boils at about  $300^\circ$ , being resolved at the same time into trichloride of carbon and chloride of trichloroacetyl,  $\text{C}^2\text{Cl}^4\text{O} = \text{C}^2\text{Cl}^4 + \text{C}^2\text{Cl}^4\text{O}$ .

Sulphuric acid acts slowly on perchlorethylic ether at  $210^\circ$  C., emitting vapours, which when condensed in water, form a solution of trichloroacetic, sulphuric, and hydrochloric acids (Malaguti). The decomposition is probably as follows:—



Potassium acts violently on perchlorethylic ether, but only near the temperature at which spontaneous decomposition begins (Malaguti). The ether is attacked by alcoholic potash, but the reaction appears to be complicated by the presence of the alcohol. (Regnault.)

An alcoholic solution of protosulphide of potassium converts perchlorethylic ether into chloroxethose (i. 924):

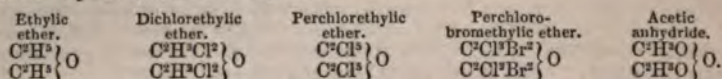


and this compound, when subjected to the action of chlorine, is reconverted into perchlorethylic ether. (Malaguti.)

*Perchlorobromethylic Ether*,  $\text{C}^2\text{Cl}^2\text{Br}^2\text{O}$ , Bromide of Chloroxethose.—Obtained by exposing chloroxethose to the action of bromine in sunshine (Malaguti).

Crystallises in octahedrons, isomorphous with those of perchlorethylic ether (Nicklès, *loc. cit.*). Colourless, inodorous. Specific gravity = 2.5 at 18° C. Melts at 96°, and is resolved at the same time into bromine and chloroxethose. The same decomposition takes place under the influence of sulphides. (Malaguti.)

This compound and the preceding exhibit towards ethyl ether and acetic anhydride, relations similar to those previously noticed with respect to dichlorethylic ether and its sulphuretted derivatives; thus:



The interest of these relations is increased by the facility with which perchlorethylic ether is converted into compounds of the acetic acid series, e.g. chloride of trichlor-acetyl and trichloracetic acid.

*Double Ethers containing Ethyl: Ethylates.*

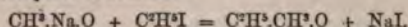
ETHYLATE OF AMYL.  $\text{C}^7\text{H}^{16}\text{O} = \begin{matrix} \text{C}^2\text{H}^2 \\ \text{C}^5\text{H}^{11} \end{matrix} \left\{ \begin{matrix} \text{O} \\ \text{O} \end{matrix} \right\}$ .—See AMYL, OXIDE OF (i. 205).

ETHYLATE OF CETYL.  $\text{C}^{18}\text{H}^{38}\text{O} = \begin{matrix} \text{C}^2\text{H}^2 \\ \text{C}^{16}\text{H}^{28} \end{matrix} \left\{ \begin{matrix} \text{O} \\ \text{O} \end{matrix} \right\}$ .—See CETYL, OXIDE OF (i. 842).

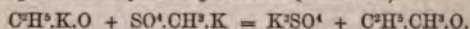
ETHYLATE OF BENZYLENE.  $\text{C}^{11}\text{H}^{16}\text{O}^2 = \begin{pmatrix} \text{C}^2\text{H}^2 \\ \text{C}^9\text{H}^6 \end{pmatrix}^2 \left\{ \begin{matrix} \text{O}^2 \\ \text{O}^2 \end{matrix} \right\}$ .—See BENZYLENIC ETHERS (i. 578).

ETHYLATES OF ETHYLENE.  $\begin{pmatrix} \text{C}^2\text{H}^2\text{H} \\ \text{C}^2\text{H}^4 \end{pmatrix} \left\{ \begin{matrix} \text{O}^2 \\ \text{O}^2 \end{matrix} \right\}$  and  $\begin{pmatrix} \text{C}^2\text{H}^2 \\ \text{C}^2\text{H}^2 \end{pmatrix}^2 \left\{ \begin{matrix} \text{O}^2 \\ \text{O}^2 \end{matrix} \right\}$ .—See ETHYLENE, OXIDE OF (p. 579).

ETHYLATE OF METHYL.  $\text{C}^3\text{H}^6\text{O} = \begin{matrix} \text{C}^2\text{H}^2 \\ \text{CH}^2 \end{matrix} \left\{ \begin{matrix} \text{O} \\ \text{O} \end{matrix} \right\}$ . *Methylate of Ethyl; Ethylmethylic, Methylethylic, or Vinomethylic Ether; Vinomethylide.* (Williamson [1850], Phil. Mag. [3] xxxvii. 350; Chem. Soc. Qu. J. iv. 106, 229.—Chancel, Compt. rend. xxxi. 152.)—Produced: 1. By the action of iodide of methyl on ethylate of sodium, or of iodide of ethyl on methylate of sodium:



The second process is to be preferred, because the product is more easily purified by rectification than in the first. The apparatus should be arranged so that the distillate may constantly flow back into the retort till the decomposition is finished; the double ether may then be distilled off from the fixed products (Williamson).—2. By the action of methylsulphate on ethylate of potassium (Chancel):



It is a transparent, colourless, very mobile liquid, boiling at 11° C. Vapour-density = 2.158, corresponding with a condensation to 2 vol. (Williamson). The vapour has a peculiar ethereal odour, and is highly inflammable. (Chancel.)

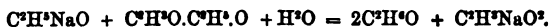
ETHYLATE OF OCTYL.  $\text{C}^{18}\text{H}^{38}\text{O} = \begin{matrix} \text{C}^2\text{H}^2 \\ \text{C}^{16}\text{H}^{28} \end{matrix} \left\{ \begin{matrix} \text{O} \\ \text{O} \end{matrix} \right\}$ . *Ethyl-octylic ether.* (Wills, Chem. Soc. Qu. J. vi. 312.)—Produced by the action of octylate of sodium on iodide of ethyl. It is a colourless mobile liquid, having a specific gravity of 0.791 at 16° C., and boiling at 177°. Vapour-density by observation = 5.095; by calculation from the preceding formula (2 vol.) = 5.47.

Wills regards this compound as *ethyl-heptylic ether*,  $\text{C}^{18}\text{H}^{38}\text{O} = \text{C}^2\text{H}^2.\text{C}^{16}\text{H}^{30}$ . The vapour-density, 4.99, deduced from this formula, certainly agrees better with the observed density than that deduced from the formula  $\text{C}^{18}\text{H}^{38}\text{O}$ ; and so likewise does the analysis, which gives 75.16 per cent. carbon and 14.44 hydrogen, the formula  $\text{C}^{18}\text{H}^{38}\text{O}$  requiring 75.00 C. and 13.88 H., whereas  $\text{C}^{18}\text{H}^{30}\text{O}$  requires 75.95 C. and 13.92 H. But the experiments of Bouis and others tend to show that castor-oil alcohol, from which this compound is derived, contains 8 rather than 7 at. carbon. (See ALCOHOLS, i. 98; also OCTYLIC ALCOHOL.)

ETHYLATE OF POTASSIUM.  $\text{C}^2\text{H}^4\text{KO}$ . *Potassium-alcohol.*—Produced by treating absolute alcohol with potassium; 1 at. hydrogen is then given off and its place supplied by potassium. The ethylate of potassium separates from the saturated liquid in colourless crystals, which, if protected from moisture and carbonic acid, may be preserved without alteration. Water converts the compound into alcohol and hydrate of potassium. Its other reactions are similar to those of the following compound.

**ETHYLATE OF SODIUM.**  $C^2H^3NaO$ . *Sodium-alcohol*.—Produced like the potassium-compound.—Crystallises in broad laminae. This compound, and the preceding, exhibit precisely similar reactions, and both form very convenient reagents for the preparation of a great number of organic bodies, serving to introduce ethyl by substitution into many compounds. Ethylate of sodium is, however, generally preferred to the potassium-compound, because sodium is cheaper than potassium, and acts less violently upon alcohol.

Ethylate of sodium, treated with the *iodide, bromide, or chloride* of an alcohol-radicle, forms iodide, bromide, or chloride of sodium, and an ether containing one or two alcohol-radicles, according to the particular reagent used (Williamson, *loc. cit.*). With *nitrate of ethyl* it acts in like manner, yielding ethylic ether, and nitrate of sodium; but with the ethers of organic acids, a different reaction takes place. With *acetate of ethyl* it forms a very insoluble compound, which absorbs water greedily from the air, yielding alcohol and acetate of sodium:



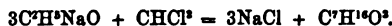
*Benzoate and oxalate of ethyl* act upon it in a somewhat similar manner (Beilstein, Ann. Ch. Pharm. cxii. 121).—*Carbonic anhydride* passed into a solution of ethylate of sodium forms a white precipitate of ethyl-carbonate of sodium (Beilstein, *loc. cit.*).—*Carbonic oxide* does not act on ethylate of sodium (Wanklyn, Ann. Ch. Pharm. cx. 111) unless a trace of moisture is present; in which case a small quantity of formic acid is produced by the action of the carbonic oxide on hydrate of sodium. (Geuther, *ibid.* cix. 73; Lieben, *ibid.* cxii. 326.)

*Cyanate of ethyl*, heated in a sealed tube with ethylate of sodium, generally yields triethylamine; sometimes, however, the greater part of the cyanate is converted into cyanurate, which acts on the ethylate of sodium in the manner explained on page 293, yielding hydrate of carbetriethyltriamine. (Hofmann, Proc. Roy. Soc. xi. 282.)

With *iodoform*, ethylate of sodium yields iodide of methylene and a body having the composition of aldehyde:



With *iodine*, it yields iodide of sodium, formate of sodium, and iodoform; which last compound acts upon it in the manner just mentioned. *Chloroform* converts ethylate of sodium into chloride of sodium, and a body having the composition  $C^2H^4O^2$ :



(Kay, Chem. Soc. Qu. J. vii. 224.)—Wurtz (Compt. rend. xliii. 478) suggests that this compound may be the triethylic ether of a triatomic alcohol homologous with glycerin;  $C^2H^4O^2 = \left\{ \begin{smallmatrix} CH \\ C^2H^3 \end{smallmatrix} \right\} O^2$ .

With *monochloroacetic acid*, ethylate of sodium yields the sodium-salt of ethylox-acetic acid (an acid isomeric with ethylglycollic acid), together with alcohol and chloride of sodium:



(Heintz, Pogg. Ann. cix. 301; Jahresber. d. Chem. 1869, p. 360.—See **OXACETIC ACID**.)

With *nitrobenzene*, ethylate of sodium (and likewise alcoholic potash) yields azobenzene, azoxybenzene, phenylamine, oxalic acid, and other products. (Béchamp and Saint-Pierre, Compt. rend. xlvii. 24.)

**ETHYLATE OF TETRYL.**  $C^2H^4O = \left\{ \begin{smallmatrix} C^2H^3 \\ C^2H^3 \end{smallmatrix} \right\} O$ , *Ethylate of Butyl, Ethyl-tetrylic or Ethyl-butylic ether*. (Wurtz, Ann. Ch. Phys. [3] xlii. 129).—Produced by the action of iodide of ethyl on tetrylate of potassium,  $C^2H^3KO$ . Colourless, mobile, fragrant liquid, of specific gravity 0.751, boiling between 78° and 80° C.

**ETHYL PHOSPHIDES OF.** See **PHOSPHORUS-BASES**.

**ETHYL PLUMBIDES OF.** See **PLUMBETHYLS**.

**ETHYL, SELENHYDRATE OF.**  $C^2H^3Se = \begin{smallmatrix} CH^2 \\ H \end{smallmatrix} Se$ , *Selenium-mercaptan*. (Wöhler and Siemens, Ann. Ch. Pharm. lxi. 360.)—This compound is obtained by saturating aqueous potash with selenhydric acid gas in an apparatus filled with hydrogen, and distilling the resulting solution of selenide of hydrogen and potassium with concentrated ethylsulphate of potassium, the air being as much as possible ex-



cluded. Selenhydric acid gas is first given off, and afterwards water passes over, together with a heavy, yellow, intolerably stinking liquid. This liquid, after being separated from the watery distillate, is placed in contact with chloride of calcium and distilled into a fresh receiver, whereupon selenium-mercaptan passes over first, and afterwards selenide of ethyl.

Selenium-mercaptan is a thin, transparent, colourless liquid, heavier than water, and insoluble therein, but soluble in alcohol. It boils considerably above  $100^{\circ}\text{C}.$ , and has an extremely repulsive odour, resembling that of the cacodyl-compounds.

It burns with a bright blue flame, giving off thick white and red vapours of selenious acid and selenium. The vapour passed through a tube heated to low redness is decomposed, with separation of selenium. A mixture of selenium-mercaptan and chloride of potassium takes fire and explodes on the addition of hydrochloric acid. Selenium-mercaptan appears not to be completely oxidised by chlorine or nitric acid. When passed in the state of vapour over red-hot copper wire, it is completely decomposed, forming crystalline selenide of copper, emitting an odour like that of benzene, and depositing a small quantity of charcoal.

In contact with mercuric oxide, it becomes heated, makes a hissing noise, and forms a yellow, easily fusible substance, which dissolves in hot alcohol, and separates from it in an amorphous condition on cooling. The alcoholic solution of selenium-mercaptan also forms a thick yellow precipitate with mercuric chloride.

**ETHYL, SELENIDE OF, or SELENETHYL.**  $\text{C}^{\text{H}}^{\text{10}}\text{Se} = (\text{C}^{\text{H}}^{\text{3}})^2\text{Se}$ . Selenhydric or Hydroselenic ether. (Löwig, Pogg. Ann. xxxvii. 552; *Chemie der organischen Verbindungen*, Aufl. 2, ii. 432.—Joy, Ann. Ch. Pharm. lxxxvi. 35.—Gm. viii. 356.)

Finely powdered selenide of potassium mixed to the consistence of a thick paste, with pure oxalic ether, then gently heated in a retort for some hours, and afterwards distilled, yields a liquid which smells and tastes like sulphide of ethyl, and when set on fire burns with an odour of horse-radish, and deposits selenium. (Löwig.)—Joy obtains the compound by distilling selenide of potassium with aqueous ethylsulphate of calcium. It appears also to be produced in small quantity, in the preparation of selenium-mercaptan. (Siemens, Ann. Ch. Pharm. lxi. 360.)

Selenethyl is a clear, pale-yellow liquid, having a most insufferable odour; it is much heavier than water, and does not mix with it. When set on fire, it burns continuously, emitting red vapours of selenium.

Selenethyl is an organic basis forming definite salts with acids. Nitric acid converts it into a nitrate, from which the chloride, bromide, and iodide may be obtained by double decomposition. (Joy.)

*Bromide of Selenethyl*, separates in the form of a lemon-yellow oil, heavier than water, when a solution of the nitrate is mixed with hydrobromic acid. It dissolves readily in ammonia, and forms an oxybromide. (Joy.)

*Chloride of Selenethyl*.  $\text{C}^{\text{H}}^{\text{10}}\text{SeCl}$ .—The solution of selenide of ethyl in nitric acid mixed with hydrochloric acid becomes milk-white, and immediately afterwards deposits drops of an oily body which is the chloride of selenethyl. It is a transparent light yellow liquid which sinks in water; when quite pure, it appears to be inodorous. It is somewhat soluble in water and more so in hydrochloric acid, which circumstance renders some care necessary in preparing it.

On leaving it for a considerable time in contact with the liquid containing hydrochloric and nitric acid, in which it has been produced, a number of well-defined transparent and colourless crystals are formed at the separating surface of the two liquids. These crystals dissolve readily in water and alcohol, and separate unchanged on evaporation. The aqueous solution is acid, and forms with ammonia a crystalline mass, from which the ammonia is separated by potash. Sulphurous acid added to it separates selenethyl. The crystals give by analysis 13.7 per cent. carbon, 4.3 hydrogen, and 20.05 chlorine: therefore 1 at. chlorine to 2 at. carbon.

*Iodide of Selenethyl*,  $\text{C}^{\text{H}}^{\text{10}}\text{SeI}$ , is obtained on adding hydriodic acid to a solution of the chloride or nitrate, as a black liquid, having a semi-metallic lustre, sinking in water. It is inodorous, does not solidify at  $0^{\circ}\text{C}.$ ; dissolves only in ammonia.

*Nitrate of Selenethyl* is formed by dissolving selenethyl in hot, moderately strong nitric acid, the action being attended with evolution of nitric oxide gas.

*Oxychloride of Selenethyl*.  $\text{C}^{\text{H}}^{\text{20}}\text{Se}^2\text{Cl}^2\text{O} = \frac{\text{C}^{\text{H}}^{\text{10}}\text{SeCl}}{\text{C}^{\text{H}}^{\text{10}}\text{SeCl}}\text{O}$ ? Chloride of selenethyl dissolves readily in ammonia, forming chloride of ammonium and oxychloride of selenethyl. The latter may be extracted by absolute alcohol, and crystallises in highly lustrous, colourless cubes, generally grouped in stellate masses. Hydrochloric acid added to the aqueous solution throws down the oily chloride of selenethyl; and sulphurous acid throws down a fetid mixture of selenethyl and the chloride. (Joy.)

**ETHYL, STANNIDES OF.** See STANNETHYLS.

**ETHYL, SULPHIDES OF.** Three sulphides of ethyl are known, viz. the proto-, di-, and tri-sulphide. They are oily liquids having a pungent alliaceous odour.

**Protosulphide of Ethyl.**  $(C^2H^5)_2S$ . *Sulphydic or Hydrosulphuric ether.* (Döbereiner, Schw. J. lxi. 377.—Regnault, Ann. Ch. Phys. [2] lxxi. 387.—Loir, Compt. rend. xxvi. 195.—Riche, Ann. Ch. Phys. [3] xliii. 297.)—This compound, the analogue of common ether, is produced by the action of protosulphide of potassium on ethylsulphate of potassium, chloride of ethyl, and other ethyl-compounds; also, according to Döbereiner, by dissolving protosulphide of iron in a mixture of strong hydrochloric acid and alcohol.

*Preparation.*—An alcoholic solution of potash is divided into two equal parts: one part is saturated with sulphydic acid gas, and then mixed with the other; the liquid is introduced into a tubulated retort; vapour of hydrochloric ether is passed through it to saturation; and heat is then gradually applied, the stream of hydrochloric ether vapour being still kept up. From the distillate, which contains alcohol as well as sulphide of ethyl, the sulphide of ethyl is precipitated by water; it is then purified by washing with water, dehydrated by chloride of calcium, and rectified (Regnault). Baudrimont (Compt. rend. liv. 616) distils sulphide of potassium with iodide of ethyl. Löwig distils sulphide of potassium with ethylsulphate of barium.

*Properties.*—Sulphide of ethyl is a colourless oily liquid having a very pungent, disagreeable, alliaceous odour. Specific gravity = 0.825 at 20° C. Boiling point 73° C. Vapour-density 3.00 (Regnault); calculated (2 vol.) = 3.12. It is insoluble in water, but soluble in alcohol.

It is very inflammable and burns in the air with a blue flame. When poured into chlorine gas, it takes fire spontaneously. Nitric acid oxidises it readily, converting it partly into ethyl-sulphurous acid  $(SO)^{\cdot}C^2H^5.H.O^2$ . It is not decomposed by boiling with potash-ley, but on distilling it over hydrate of potassium sulphide of potassium is formed, and alcohol passes over, together with undecomposed sulphide of ethyl,  $(C^2H^5)_2S + 2KHO = K_2S + 2(C^2H^5.H.O)$ . It is not altered by mercuric oxide, but forms a yellow precipitate with acetate of lead.

*Compounds of Ethylic Sulphide with Metallic Chlorides.*

**Mercury-compound.**  $(C^2H^5)_2S.2HgCl$ , or  $(C^2H^5)_2S.Hg^2Cl^2$ .—By agitating aqueous mercuric chloride with sulphide of ethyl or its alcoholic solution, a crystalline compound is obtained, which may be purified by recrystallisation from boiling alcohol, and obtained in distinct crystals by solution in ether or wood-spirit. It forms monoclinic prisms, in which  $\infty P : \infty P = 103^{\circ} 40'$ ;  $\infty P : oP = 73^{\circ} 10'$ . It is heavier than water; has a very unpleasant odour; becomes opaque and gives off sulphide of ethyl on exposure to the air; melts at 90° C. to a colourless liquid, which solidifies to a crystalline mass on cooling; and decomposes at a stronger heat, emitting fetid vapours. (Loir.)

**Platinum-compound**  $(C^2H^5)_2S.PtCl^2$ .—Obtained like the preceding, which it resembles in most of its properties. Melts at 108° C.

*Chlorinated Derivatives of Ethylic Sulphide.*

Sulphide of ethyl takes fire when poured into chlorine gas; but when dry chlorine is passed into a flask containing sulphide of ethyl, not at first into the liquid, the vessel being kept cool and in the shade, substitution-products are formed, the chlorine quickly disappears, and hydrochloric acid gas is abundantly evolved; towards the end of the operation, the chlorine may be passed directly into the liquid. With about 15 grammes of liquid, the operation is completed in diffused daylight in about four hours. (Riche.)

To separate the products, the liquid is first heated to 70°—80° C., while a stream of carbonic anhydride is passed through it, whereby chlorine and hydrochloric acid are expelled, and then distilled. It begins to boil at 160° C., the greater portion distils over between 163° and 173°, and the boiling point afterwards rises to 230°; but the liquid then begins to decompose, giving off hydrochloric acid and leaving a carbonaceous residue (Riche). The only definite compound obtained from it is:

**Dichlorethylic Sulphide.**  $(C^2H^4Cl^2)_2S$ .—This compound forms the greater part of the distillate, passing over between 163° and 173°, and may be purified by rectification. It is a light-yellow liquid of specific gravity 1.547, having a strong unpleasant odour, boiling between 167°—172° C. It is decomposed by hydrogen and by protosulphide of potassium, with formation of viscid products. (Riche.)

**Trichlorethylic Sulphide.**  $(C^2H^3Cl^3)_2S$ .—If the chlorine is allowed to act on



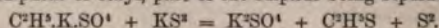
the sulphide of ethyl in diffused daylight without external cooling, a liquid is obtained, blackish at first, becoming deep yellow afterwards, from which, by fractional distillation, this and the following compounds are obtained.

Trichlorethylic sulphide is a dark yellow oil, boiling between  $189^{\circ}$  and  $192^{\circ}$  C. (Riche.)

**Tetrachlorethylic Sulphide.**  $(C^2HCl^4)^2S$ .—This compound, previously obtained by Regnault, passes over in the distillation between  $217^{\circ}$  and  $222^{\circ}$  C. It may be obtained in larger quantity by passing chlorine for a long time, and in large excess, over sulphide of ethyl, heating the liquid ultimately to between  $60^{\circ}$  and  $80^{\circ}$  C. It is a yellow liquid of intolerable odour, of specific gravity 1.673 at  $24^{\circ}$  C., boiling, according to Regnault, at about  $160^{\circ}$  C. with partial decomposition.

**Perchloroethylic Sulphide.**  $(C^2Cl^3)^2S$  (?)—By the action of chlorine on ethylic sulphide in sunshine. Trichloride of carbon is then formed and a liquid obtained, which is probably  $(C^2Cl^3)^2S$ ; but it has not been analysed. (Riche.)

**Disulphide of Ethyl.**  $C^2H^4S_2$ , or  $C^4H^{10}S^2$ . *Thialol.* (Zeise, Pogg. Ann. xxxi. 371.—Pyr. Morin, *ibid.* xlviii. 483.—Löwig, *ibid.* xxvii. 550.—Löwig and Weidmann, *ibid.* xlix. 326.—Cahours, Ann. Ch. Phys. [3] xviii. 268.—Muspratt, Chem. Soc. Qu. J. iii. 19.)—Produced: 1. By the action of ethyl-sulphate of potassium on disulphide of potassium in concentrated aqueous solution (Zeise). If the solution also contains trisulphide of potassium, a certain quantity of trisulphide of ethyl is formed at the same time; nevertheless the greater part of the trisulphide of potassium likewise yields disulphide of ethyl, part of the sulphur being separated:



2. By distilling oxalate of ethyl with disulphide of potassium.—3. By decomposing

sulphosulphite of ethyl,  $\begin{smallmatrix} SO \\ (C^2H^4)^2 \end{smallmatrix} \begin{smallmatrix} O \\ S \end{smallmatrix}$ , a product of the imperfect oxidation of mercaptan by nitric acid (see SULPHUROUS ETHERS), with potash (Löwig and Weidmann).—4. By the dry distillation of ethyl-sulphocarbonate of potassium. (Zeise.)

**Preparation.**—1. A mixture of 1 pt. disulphide and 2 pts. ethylsulphate of potassium (or 3 pts. ethylsulphate of potassium and 2 pts. ordinary liver of sulphur) is distilled in a retort with 5 pts. water; more water is added when the residue becomes thick; the distillation is continued; and this treatment is repeated three or four times, as long as oil continues to pass over. The yellow and still impure disulphide of ethyl is separated from the water which has passed over with it, shaken up several times with large quantities of fresh water, and dried for several days over chloride of calcium. Of this oil, which is contaminated with a more fixed oil (hence its boiling point rises from  $150^{\circ}$  to  $200^{\circ}$  C.), a quantity is distilled off sufficient to raise the boiling point to  $190^{\circ}$ ; the distillate is again distilled till the boiling point rises to  $180^{\circ}$ ; and this treatment is repeated till a distillate is obtained, which passes over at  $151^{\circ}$  without leaving any residue. The quantity of the pure product thus obtained is about half that of the impure oil.—2. Muspratt distils together in a large retort equal portions of the concentrated solutions of ethylsulphate of calcium and trisulphide of potassium; washes the oily product repeatedly with distilled water; and then rectifies it several times over chloride of calcium.

**Properties.**—Disulphide of ethyl is a colourless oily liquid, insoluble in water, soluble in alcohol and ether. Its specific gravity is about equal to that of water, so that it first floats upon water, and then, perhaps from absorbing water, sinks to the bottom. It boils at  $151^{\circ}$  C., passing over undecomposed. It is neutral to vegetable colours; has a very strong and repulsive alliaceous odour (according to Muspratt it has a most disgusting smell when crude, but after rectification the smell is only slightly alliaceous); when inhaled it is very apt to produce headache; tastes first sharp and afterwards sweetish; 10 drops of it given to a rabbit cause convulsive movements, from which, however, the animal slowly recovers. Vapour-density = 4.270 (Cahours). If then its molecule in the state of vapour is condensed to 2 vols., according to the ordinary law, the rational formula must be  $C^4H^{10}S^2$ , not  $C^2H^4S$ : for  $(2.12 + 5.1 + 32) \times 0.693 = 4.227$ .

**Decompositions.**—1. Disulphide of ethyl is very inflammable, and burns with a blue flame. It is not altered by exposure to the air. Chlorine decomposes it readily, especially in sunshine (Cahours). With bromine it forms a compound, soluble in water, which yields, by distillation, hydrobromic acid and an aromatic liquid. Fuming nitric acid converts it into ethylsulphurous acid, a small quantity of sulphuric acid being also formed. Strong sulphuric acid does not dissolve it in the cold; on applying heat, decomposition takes place, attended with evolution of sulphurous anhydride. With mercuric oxide, disulphide of ethyl slowly forms a yellow mass. The alcoholic solution precipitates mercuric chloride white, acetate of lead yellowish white. (Morin.)



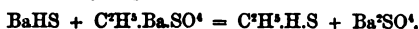
**Trisulphide of Ethyl.**  $(C^2H^5)_3S^3$ .—Obtained, together with the disulphide, by distilling a mixture of ethylsulphate and pentasulphide of potassium. On rectifying the product, the disulphide passes over first, and afterwards the trisulphide. It is a heavy, oily liquid, which reacts like the disulphide with nitric acid and with chlorine. (Cahours, *loc. cit.*)

**Pentasulphide of Ethyl.**  $(C^2H^5)_5S^5$  (?)—This appears to be the composition of a white, sweet-tasting, fusible sulphuretted compound, precipitated by water from an alcoholic solution of oxalic ether and pentasulphide of potassium. (Löwig, *Chemie der Organischen Verbindungen*, i. 464.)

**ETHYL, SULPHYDRATE OF.**  $C^2H^5S = \begin{matrix} C^2H^5 \\ H \end{matrix} \} S$ . *Hydrosulphate of Ethyl.*

*Sulphethyle or Ethylsulphide of Hydrogen. Mercaptan.*—This body, which has the composition of alcohol in which the oxygen is replaced by sulphur, was discovered by Zeise in 1833 (Pogg. Ann. xxxi. 369), and has been further examined by Liebig (Ann. Ch. Pharm. xi. 10; xxiii. 34), Debus (*ibid.* lxxii. 18), Regnault (Ann. Ch. Phys. [2] lxxi. 390), and others. (See also Gm. viii. 340; Gerh. ii. 284.) The name mercaptan, by which it is generally known, signifies *corpus mercurio aptum*, a body having a strong tendency to unite with mercury.

Mercaptan is produced in numerous cases of the reaction of ethyl-compounds with metallic sulphydrates, especially with those of the alkali-metals: 1. By the action of sulphydrate of barium on ethylsulphate of barium or of calcium:



By the action of chloride of ethyl on sulphydrate of potassium:



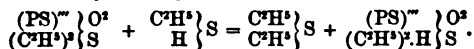
3. By the dry distillation of xanthate of potassium.—4. By the action of nitrate of ethyl on sulphydrate of ammonium. (E. Kopp.)

*Preparation.*—1. Crystallised ethylsulphate of calcium is distilled with a solution of sulphydrate of barium; the product is collected in a well cooled receiver; the aqueous portion is decanted; and the mercaptan which remains is purified by distillation with a small quantity of mercury, then dehydrated by chloride of calcium (Zeise).—2. A mixture of alcohol and sulphuric acid, such as is used for preparing the ethylsulphates, is saturated with potash; and the liquid, decanted from the precipitated sulphate of potassium, is mixed with excess of caustic potash, then saturated with sulphuretted hydrogen and distilled (Wöhler).—3. An alcoholic solution of potash is saturated with sulphuretted hydrogen, and then treated with vapour of chloride of ethyl. Baudrimont (Compt. rend. liv. 616) recommends iodide of ethyl for this purpose, instead of the chloride, because it is less volatile.

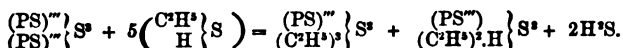
*Properties.*—Mercaptan is a colourless, very mobile liquid having a peculiarly offensive alliaceous odour. Specific gravity 0.8326 at 21° C. (Liebig). Boils between 61° and 63° C. Vapour-density = 2.11 (Bunsen); by calculation (2 vol.) = 2.148. It is very inflammable and burns with a blue flame. When a drop of it at the end of a glass rod is briskly agitated, it solidifies by the cold produced by its own evaporation. It is neutral to vegetable colours, very sparingly soluble in water, but dissolves in all proportions in alcohol and ether. It dissolves sulphur, phosphorus, and iodine.

*Decompositions.*—1. Mercaptan, boiled with moderately strong nitric acid, acquires a red colour, and after a while deposits a peculiar oil. On continuing the ebullition, the oil disappears and ultimately ethylsulphurous acid is obtained.

2. Mercaptan, heated in a sealed tube with triethyllic disulphophosphate, yields sulphide of ethyl and diethyllic disulphophosphate:



3. With pentasulphide of phosphorus, it forms triethyllic and diethyllic tetrasulphophosphates:

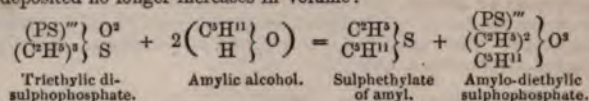


(L. Carus, Ann. Ch. Pharm. cxii. 190.)

4. Potassium and sodium eliminate hydrogen from mercaptan in the same manner as from alcohol, and form analogous substitution-products, viz. the sulphethyldates of potassium and sodium.—5. The alcoholic solution of mercaptan precipitates many metallic salts, forming a yellow precipitate with lead-salts, and white precipitates with cupric acetate, mercuric salts, and trichloride of gold. These precipitates, which are formed from mercaptan by the substitution of a metal for one atom of hydrogen, and

have the general formula  $C^2H^3.M.S.$  are called Sulphethyates, Ethylsulphides, or Mercaptides. This general formula likewise includes certain double sulphur-ethers analogous to the double ethylic ethers (p. 642).

*Sulphethylate of Amyl*,  $C^2H^3.S = C^2H^3.C^3H^{11}.S.$  — Prepared by heating 1 at. triethylic disulphophosphate with 2 at. amyl alcohol to  $150^\circ C.$  till the vitreous mass which is deposited no longer increases in volume:

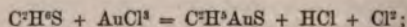


The ethereal liquid which floats on this mass is decanted and distilled; the liquid which passes over between  $120^\circ$  and  $140^\circ C.$  is dissolved in several times its volume of alcohol and precipitated by water; this treatment is repeated several times; and the product is finally washed with water till it is quite free from amyl alcohol.

Sulphethylate of amyl is a colourless liquid, smelling like sulphide of ethyl, and sulphide of amyl. It boils at  $132^\circ$ — $133.5^\circ C.$  (corrected), under a pressure of  $75.8$  mm. Vapour-density, obs. =  $4.4954$ ; calc. =  $4.5606$ . Its alcoholic solution forms a white precipitate with an alcoholic solution of mercuric chloride. (Carius, Ann. Ch. Pharm. exix. 315; Rép. Chim. pur. C. 1862, p. 172.)

*Sulphethylate of Copper* is obtained as a white gelatinous precipitate on mixing the alcoholic solutions of mercaptan and cupric acetate; also, as a nearly colourless mass, by digesting finely pulverised cupric oxide with mercaptan in a closed vessel. The salt when dry burns in the flame of a candle with a bluish-green light. It is not decomposed by boiling potash; forms a colourless solution with moderately strong hydrochloric acid; and dissolves sparingly in alcohol.

*Sulphethylate of Gold*.  $C^2H^3.AuS.$ —Obtained as a white gelatinous precipitate on mixing the dilute alcoholic solutions of auric chloride and mercaptan (1 pt. mercaptan dissolved in 70 pts. alcohol with 1 pt. chloride of gold in 20 pts. alcohol). Solid trichloride of gold is violently attacked by mercaptan, the mass becoming very hot and giving off large quantities of hydrochloric acid. Oxide of gold is still more violently attacked, the mercaptan sometimes taking fire, and a black instead of a white product being obtained. As the compound produced in these reactions is not  $(C^2H^3)^2Au''S^2$ , but  $C^2H^3AuS$ , it follows that chlorine or oxygen must be set free, as shown by the equation:



and this, acting on another portion of the mercaptan, doubtless gives rise to the great heat evolved when the materials are used in the undissolved state.

Sulphethylate of gold remains white when heated to  $190^\circ C.$ ; at  $225^\circ$  it begins to turn brown and gives off a yellowish liquid (probably disulphide of ethyl), unaccompanied by gas, and leaves metallic gold. It is not decomposed by potash, or by sulphuric or hydrochloric acid. Nitric acid decomposes it, with violent evolution of gas.

*Sulphethylate of Lead*, obtained by precipitation from alcoholic solutions of mercaptan and acetate of lead, is white, crystalline, soluble in excess of the lead-solution. It blackens by heat; does not appear to be decomposed by potash. Nitrate of lead is not precipitated by mercaptan.

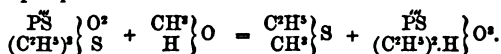
*Sulphethylate of Mercury* (mercuricum).  $C^2H^3.HgS$ , or  $(C^2H^3)^2.Hg''S^2$  (according as the atomic weight of mercury is taken at 100 or 200).—This compound is quickly formed on bringing mercuric oxide in contact with mercaptan, either pure or dissolved in alcohol, the action being attended with great evolution of heat. It is a white, crystalline mass, unctuous to the touch, melting at  $85^\circ C.$ , inodorous even in the melted state. It dissolves in 12 or 15 pts. alcohol of 85 per cent., and separates on cooling in white scales having a silvery lustre. When heated above its melting point, it turns yellow, exhales an intoxicating odour, and gives off metallic mercury. At  $130^\circ C.$  it gives off an oil, which appears to be disulphide of ethyl.

Sulphethylate of mercury is not decomposed by aqueous potash; but aqueous sulphide of potassium separates sulphide of mercury from it, forming a solution which contains the sulphethyates of potassium and of mercury, probably combined in a double salt. This solution, when boiled and evaporated, yields a white precipitate; on addition of lead-salts, a yellow precipitate; with sulphide of potassium, a grey, insoluble compound. Sulphydic acid decomposes it completely, forming sulphide of mercury and sulphydrate of ethyl. Dilute hydrochloric acid dissolves it slowly at the boiling heat, and deposits it again on cooling in crystals having a strong lustre. Strong nitric acid decomposes it, with violent evolution of nitrous vapours, forming a solution from which water throws down a colourless oil. Metallic lead immersed in the melted

salt throws down metallic mercury and forms sulphide of ethyl, sulphide of lead, and lead-amalgam.

A compound of *sulphethylete* and *chloride of mercury*,  $C^2H^3HgS.HgCl$ , is obtained, on mixing an alcoholic solution of mercaptan with mercuric chloride, as a white bulky precipitate, changing after a while to a mass of crystalline laminae. It is but sparingly soluble in water and in ether; boiling alcohol dissolves it somewhat more freely, and deposits it in thin crystalline laminae on cooling. (Debus.)

*Sulphethylete of Methyl*,  $C^2H^3S = C^2H^3.CH^3.S$ .—This compound, the analogue of Williamson's ethylmethyl ether (p. 542), is obtained by heating a mixture of triethylic disulphophosphate with twice its volume of methyl alcohol in a sealed tube to  $150^\circ C.$ , care being taken not to exceed that temperature. The reaction is complete in a few hours, the tube then containing a brownish ethereal liquid, which is nearly pure sulphethylete of methyl, and a nearly colourless, vitreous mass, consisting of diethylic sulphophosphate:



The reaction is always attended with the formation of secondary products, resulting chiefly from the decomposition of the diethylic sulphophosphate.

*Sulphethylete of methyl*, purified by rectification, is a colourless, very mobile liquid, having an odour more like that of methyl than of ethylic sulphide. It boils at  $58.8^\circ$ — $59.5^\circ C.$  (corrected) under a pressure of 787 mm. Vapour-density, observed = 2.609; calculated = 2.6258. It forms crystalline compounds with metallic chlorides. Its alcoholic solution, mixed with alcoholic mercuric chloride, forms a precipitate consisting of small scales having the composition  $C^2H^3S.2HgCl$ . (Carius, *loc. cit.*)

*Sulphethylete of Platinum*,  $C^2H^3PtS$ , is a light yellow, muddy precipitate, obtained by mixing the alcoholic solutions of mercaptan and dichloride of platinum, the latter not in excess.

*Sulphethylete of Potassium* is produced by the action of potassium on mercaptan (sulphethylete of hydrogen). It is a dull white granular mass, very soluble in water, less soluble in alcohol. It may be heated considerably above  $100^\circ C.$  without decomposing, but a very strong heat carbonises it. Its aqueous solution likewise decomposes and blackens on exposure to the air. *Hydrochloric* and *dilute sulphuric acids* decompose it, with brisk effervescence. The recently prepared aqueous solution precipitates *lead-salts*, yellow in the cold, white on boiling. The partially decomposed solution forms a brick-red precipitate with *silver-salts*.

*Sulphethylete of Silver* is the white precipitate formed on adding nitrate of silver to the aqueous solution of mercaptan; but it appears always to retain a portion of nitrate.

*Sulphethylete of Sodium*.—Prepared like the potassium-salt. Dissolves easily in water, forming an alkaline liquid.

#### *Zeise's Indifferent Sulphuretted Oil:*

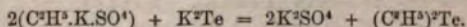
Zeise, in preparing the sulphur-compounds of ethyl, obtained, on several occasions, a peculiar oil, which he sometimes distinguishes by the epithet *indifferent*, and which differs from protosulphide of ethyl, from mercaptan, and from disulphide of ethyl.

This oil is formed in small quantity in the preparation of mercaptan from sulphhydrate of barium and an ethylsulphate, and consequently the mercaptan requires to be purified from it. In the preparation of disulphide of ethyl from disulphide of barium and an ethylsulphate, small quantities of this indifferent oil likewise pass over with the disulphide of ethyl. It is however obtained in greatest abundance, mixed with about  $\frac{1}{11}$  mercaptan, by distilling 1 at. protosulphide of barium with a concentrated solution of 1 at. ethylsulphate of barium. The mixture becomes turbid at  $60^\circ C.$ , then gummy and covered with scum; at the end of the distillation, nothing remains but sulphate of barium. If too much water be added, the whole of the oil remains dissolved in the watery distillate. The oily mixture of this indifferent oil and mercaptan which passes over with the watery distillate (which is free from alcohol) begins to boil at  $70^\circ C.$ , but the boiling point gradually rises to  $102^\circ$ ; by repeated fractional distillation, it may be separated into a more volatile portion, the mercaptan, and a less volatile portion, the indifferent oil. The latter may be freed from the last portions of mercaptan by agitation with water and oxide of lead, and from water by rectification over chloride of calcium. It is a transparent, colourless, neutral oil, of specific gravity 0.8449 at  $18^\circ C.$  Its odour resembles that of mercaptan, but is weaker and less ethereal. It burns with a redder flame than mercaptan, producing a larger quantity of sulphurous anhydride. It is more soluble in water than mercaptan. Its alcoholic solution produces no turbidity in lead-



or mercury-salts. It contains 22.3 per cent. carbon, 10.8 hydrogen, and 28.0 sulphur, approximating to the formula  $C^2H^{10}SO^3 = \text{mercaptan} + 3 \text{ at. water}$ .

**ETHYL, TELLURIDE OF, or TELLURETHYL.**  $C^2H^{10}Te = (C^2H^5)^2Te$ . *Tellurhydric or Hydrotelluric Ether.* (Wöhler, Ann. Ch. Pharm. xxxv. 111; lxxxiv. 69.—Mallet, *ibid.* lxxix. 223; Chem. Soc. Qu. J. v. 71.)—This compound is formed by the action of telluride of potassium on ethylsulphate of potassium:



*Preparation.*—Telluride of potassium is prepared by mixing 1 pt. of tellurium powder with 10 pts. of burnt tartar; introducing the mixture into a porcelain retort fitted with a glass tube bent downwards at right angles; heating the retort to redness for three or four hours—as long, indeed, as carbonic oxide continues to escape; and then introducing the end of the bent tube into a flask filled with carbonic anhydride, to prevent access of air. As soon as the mixture is quite cold, a concentrated solution of ethylsulphate of potassium (3 or 4 pts. of the solid salt to 1 pt. of tellurium) prepared with water freed from air by boiling, is poured into the retort, which is then tightly corked; and the whole heated for some time, with constant agitation, to  $40^\circ$  or  $50^\circ$ . The resulting purple solution, together with the undissolved portion, is then quickly poured into a flask previously filled with carbonic anhydride; the retort again filled with the same gas; a small quantity of the solution of ethylsulphate poured into it (a portion having been kept back for the purpose); the retort again closed; and the digestion repeated. These precautions are necessary to prevent loss of telluride of potassium by oxidation. The flask is then connected with a condensing tube and receiver, and the mixture kept constantly in a state of gentle ebullition. The flask then becomes filled with the yellow vapour of tellurethyl, and that compound distils over, together with water, in which it sinks in drops. Finally, when about  $\frac{2}{3}$  of the monotelluride of ethyl has passed over, a small quantity of ditelluride is likewise obtained, differing from the former by its black-red colour.

*Properties.*—Tellurethyl is a deep yellowish-red liquid, heavier than water, and boiling below  $100^\circ$  C. It has a strong, very persistent, and extremely disgusting odour, like that of sulphide of ethyl, or telluretted hydrogen. It appears to be very poisonous. Its vapour has a deep yellow colour. It is but slightly soluble in water.

*Decompositions.*—Tellurethyl is very inflammable, and burns with a clear white flame bordered with light blue, giving off thick white fumes of tellurous acid. It remains unaltered under water, but when exposed to the air becomes covered with a yellowish, and afterwards with a white film, and is ultimately converted into a white earthy mass. In sunshine this oxidation takes place much more quickly, and is attended with slight fuming; but no fire is produced, even in oxygen gas. Tellurethyl, treated with *nitric acid*, causes violent evolution of nitric oxide, and forms a solution from which aqueous hydrochloric acid throws down a heavy colourless oil. (Wöhler.)

*Combinations.*—Tellurethyl exhibits the properties of a diatomic radicle, uniting with chlorine, oxygen, and acid radicles in general to form salts. The nitrate is obtained by treating tellurethyl with nitric acid; the other salts by double decomposition.

*Bromide.*  $C^2H^{10}TeBr^2$ .—When a solution of the nitrate or the oxychloride of tellurethyl is mixed with hydrobromic acid, the bromide separates in the form of a pale yellow, very heavy, inodorous oil.

*Chloride.*  $C^2H^{10}TeCl^2$ .—Obtained by mixing a solution of the nitrate, not containing a great excess of nitric acid, with strong hydrochloric acid in a narrow cylindrical vessel. The mixture becomes milky at first, and after a while the chloride sinks to the bottom, in the form of a heavy oil. It may be washed with water, though it is somewhat soluble in that liquid, and also in strong hydrochloric acid. When the latter solution is evaporated at a gentle heat, the chloride separates in oily drops (Wöhler, Mallet). The chloride is also precipitated as an oil on adding hydrochloric or sulphuric acid to a solution of the sulphate or oxychloride. (Wöhler.)

Transparent and colourless oil, heavier than water, and having an unpleasant odour. May be distilled without decomposition, but appears to have a very high boiling-point, for when distilled with water it passes over very slowly. Oxide of silver decomposes this compound, converting it into oxide of tellurethyl. (Mallet.)

*Fluoride.*—Hydrofluoric acid, added to solutions of the oxychloride, throws down fluoride of tellurethyl, while a soluble fluorine-compound remains in solution and may be crystallised by evaporation. The same compound is obtained by treating oxide of tellurethyl with hydrofluoric acid. (Wöhler.)

*Iodide.*  $C^2H^{10}TeI^2$ .—Formed by mixing a solution of the nitrate, oxychloride, or oxybromide with hydriodic acid, or by supersaturating the chloride with this acid. The iodide separates in the form of a very beautiful orange-coloured precipitate, which

when washed and dried forms an orange-yellow powder. Heated in water, it melts at  $50^{\circ}\text{C}$ . to a heavy, yellowish-red liquid, which, on cooling, solidifies to a yellowish-red, opaque, scaly, crystalline mass, which, like mica, may be very easily broken in the direction of the cleavage-plane. Dissolves sparingly in water, but readily in hot alcohol, from which it crystallises in long, thin, orange-yellow prisms. When heated above its melting point it decomposes, yielding a yellowish-red oil, a black sublimate, and metallic tellurium. If a partially decomposed solution of hydriodic acid be used in the preparation of this body, an almost blood-red precipitate is obtained, most probably containing a higher iodide.

*Nitrate.*  $\text{C}^{\text{H}}^{\text{I}}\text{Te}(\text{NO}_3)_2 = \left\{ \begin{smallmatrix} (\text{NO}_3)_2 \\ (\text{C}^{\text{H}}^{\text{I}}\text{Te}) \end{smallmatrix} \right\} \text{O}^2$ .—Obtained in the form of a white, crystalline mass by dissolving tellurethyl in moderately strong nitric acid, and evaporating to dryness at a gentle heat. This salt burns away like gunpowder when heated. It dissolves readily in water. Alkalis added to the solution form no precipitate, because the oxide of tellurethyl is soluble in water. Sulphurous acid separates tellurethyl in dark, red drops. Sulphuretted hydrogen throws down the sulphide (p. 283). Hydrochloric acid precipitates the chloride. (Mallet.)

*Oxalate* (basic).  $\left\{ \begin{smallmatrix} (\text{C}^{\text{H}}^{\text{I}}\text{Te})_2 \\ (\text{C}^{\text{O}}\text{O}^2)^2 \text{H}_2 \end{smallmatrix} \right\} \text{O}^2$ .—Obtained by digesting the oxychloride with water and excess of silver-oxalate. Short, transparent prisms, sparingly soluble in water, with acid reaction. When heated, it melts, boils, gives off tellurethyl, forms a crystalline sublimate, and leaves a residue of tellurium.

*Oxide.*—Not yet obtained in a state of purity, its isolation being always attended with partial decomposition. It may be obtained: 1. By direct oxidation of the alcoholic solution in the air; the process is however very slow and does not afford a good mode of preparation (Mallet).—2. By treating the chloride immersed in water, with recently precipitated oxide of silver, which immediately acts upon it with spontaneous evolution of heat, and is converted into chloride. The filtered liquid is an aqueous solution of oxide of tellurethyl free from silver and chlorine. By evaporation at a gentle heat, the oxide is obtained as a white mass, having a very distinct crystalline character (Mallet).—3. Wöhler, by digesting a solution of the crystallised oxychloride with recently precipitated oxide of silver, found that chloride of silver was immediately formed; but the liquid did not filter well, the excess of oxide of silver running through. On evaporating it in the water-bath to a syrup, it began to smell of tellurethyl, and the undissolved matter turned black. On dilution with water, it filtered clearly, but the solution, when again evaporated to a syrup, emitted an odour of tellurethyl and began suddenly to give off a gas (carbonic anhydride absorbed from the air) with effervescence.—4. A solution of the sulphate was decomposed with a hot saturated solution of baryta-water, the excess of baryta removed by carbonic acid, the liquid heated some time to expel the carbonic acid, and then filtered. The solution, when evaporated over the water-bath, smelt constantly of tellurethyl, and, as soon as it was brought down to the consistence of a syrup, gave off gas with effervescence. The same evolution of gas was subsequently produced in the cold mass by stirring it. The syrup residue exhibited signs of crystallisation. (Wöhler.)

The crystalline oxide obtained by Mallet decomposed when heated in a tube, yielding metallic tellurium and an oil having a very offensive odour. In the air it burned with the blue flame of tellurium (Mallet).—The solution of the oxide has an alkaline reaction, and when mixed with hydrochloric acid, yields chloride of tellurethyl in colourless oily drops (Wöhler, Mallet).—Yields a crystalline salt with nitric acid. (Wöhler.)

*Oxybromide.*  $\left\{ \begin{smallmatrix} (\text{C}^{\text{H}}^{\text{I}}\text{Te})_2 \\ \text{O} \end{smallmatrix} \right\} \text{Br}^2 = \text{C}^{\text{H}}^{\text{I}}\text{TeO}.\text{C}^{\text{H}}^{\text{I}}\text{TeBr}^2$ .—Obtained by dissolving the bromide in ammonia. Crystallises in shining, colourless prisms, of the same form as the oxychloride.

*Oxychloride.*  $\left\{ \begin{smallmatrix} (\text{C}^{\text{H}}^{\text{I}}\text{Te})_2 \\ \text{O} \end{smallmatrix} \right\} \text{Cl}^2 = \text{C}^{\text{H}}^{\text{I}}\text{TeO}.\text{C}^{\text{H}}^{\text{I}}\text{TeCl}^2$ .—Obtained by dissolving the chloride in caustic ammonia or potash, and evaporating the solution till it crystallises. It is better to add ammonia, because an excess of it does not decompose the product. The salt crystallises easily as the excess of ammonia evaporates. The mother-liquor contains sal-ammoniac or chloride of potassium:



Colourless, highly lustrous, six-sided prisms, soluble in water and alcohol; a solution of the compound in hot alcohol yields very beautiful crystals.



Hydrochloric acid added to solutions of this compound throws down colourless oily chloride of tellurethyl, a small quantity of which remains in solution. Sulphuric acid also precipitates the chloride, while sulphate of tellurethyl remains in solution, and from this the chloride may be precipitated by hydrochloric acid. (Wöhler.)

**Oxyiodide.**  $(C^2H^5Te)^2 \begin{Bmatrix} I^2 \\ O \end{Bmatrix}$  =  $C^2H^5TeO.C^2H^5TeI^2$ .—Obtained by dissolving the iodide in ammonia and leaving the solution to evaporate spontaneously. Crystallises readily as the ammonia volatilises, in pale-yellow transparent prisms, isomorphous with the corresponding chlorine and bromine compounds. These crystals become orange-yellow on the surface when exposed to the air. They are but sparingly soluble in pure water, but dissolve freely in water containing excess of ammonia. Hydrochloric acid added to the aqueous solution throws down a heavy, yellowish-red mixture of chloride and iodide of tellurethyl. Sulphuric acid throws down the orange-yellow iodide; and hydrochloric acid added to the filtrate separates the colourless chloride. Sulphurous acid precipitates from the solution of the oxyiodide an easily fusible, semi-solid mixture of tellurethyl and the iodide.

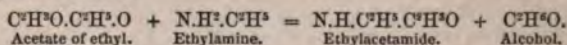
**Sulphate.**  $(C^2H^5Te)^2 \begin{Bmatrix} SO^2 \\ (SO^2)^2.H^2 \end{Bmatrix} O^4$ .—Obtained by adding a hot, neutral, saturated solution of sulphate of silver to a solution of oxychloride of tellurethyl, as long as any chloride of silver is formed.—Crystallises in groups of small, short, colourless prisms, easily soluble in water. Sulphurous acid precipitates from its solution a yellow oily body, of a most disagreeable odour. Chloride of barium throws down sulphate of barium and reproduces the oxychloride.

**Sulphide.**  $C^2H^5TeS$ .—Sulphuretted hydrogen passed through a solution of the nitrate throws down an orange-coloured precipitate, which on heating the liquid melts into black drops. (Mallet.)

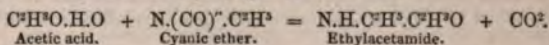
**Telluride of Tellurethyl or Ditelluride of Ethyl,**  $C^2H^5Te^2$ .—This compound was first obtained by Mallet in endeavouring to prepare telluric mercaptan by saturating an aqueous solution of telluride of potassium and ethylsulphate of barium with telluretted hydrogen, and distilling. At first nothing but tellurethyl passed over; but on applying a stronger heat, another liquid distilled over, having a much greater density and higher boiling point, and so deep a red colour, that, even in small quantity, it appeared black and opaque like bromine. It likewise possesses an extremely offensive odour. (Mallet.)

The same compound is obtained in small quantity in the preparation of tellurethyl by the method given on p. 550. When about  $\frac{2}{3}$  of the tellurethyl has passed over, a small quantity of the ditelluride likewise distils over, distinguished by its deep red colour. (Wöhler.)

**ETHYLACETAMIDE.**  $C^2H^5NO = N.H.C^2H^3.C^2H^3O$ .—Discovered by Wurtz in 1850 (Ann. Ch. Phys. [3] xxx. 491; Compt. rend. xxxvi. 180). It is obtained: 1. By adding acetate of ethyl to aqueous ethylamine, and evaporating, first over the water-bath, then in vacuo:

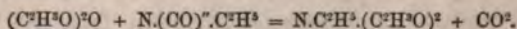


2. By the action of cyanate of ethyl on glacial acetic acid:



It is a colourless, syrupy, uncrystallisable liquid, which boils at  $200^\circ C.$ , distilling almost without decomposition. It is decomposed by potash, yielding ethylamine and acetate of potassium, and by phosphoric anhydride, with separation of carbon.

**Ethylidiacetamide.**  $C^2H^{11}NO^2 = N.C^2H^3.(C^2H^3O)^2$ . (Wurtz, Ann. Ch. Phys. [3] xlii. 43.)—Produced by heating cyanate of ethyl with acetic anhydride in a sealed tube to  $180^\circ$ — $200^\circ C.$ :



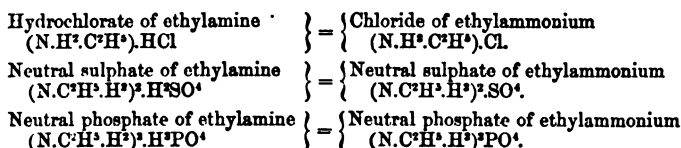
It is a colourless liquid of specific gravity 1.0092 at  $20^\circ C.$

**ETHYLAMIDE.** Syn. with ETHYLAMINE.

**ETHYLAMINES and ETHYLAMMONIUMS.** Organic bases formed on the types  $NH^3$  and  $NH^4$  respectively, by the substitution, more or less complete, of ethyl for hydrogen, viz. ethylamine,  $N.H^2.C^2H^3$ ; diethylamine,  $N.H.(C^2H^3)^2$ ; triethylamine,  $N.(C^2H^3)^3$ ; and tetrethylammonium,  $N(C^2H^3)^4$ . The first three of these com-



pounds, which are formed on the ammonia type, are known in the free state, and, like ammonia, unite directly with acids, forming salts which may be regarded as analogous in composition either to hydrochlorate of ammonia or to chloride of ammonium, *e. g.* :



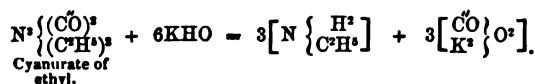
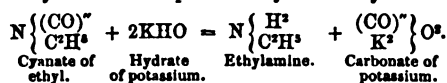
Tetretethylammonium, on the other hand, like other ammonium-bases (*i. 194*), is not known in the free state, and its salts cannot be referred to the ammonia type, excepting by regarding them as compounds of triethylamine with chloride, sulphate, &c., of ethyl, *e. g.* iodide of tetretethylammonium  $\text{N}(\text{C}^2\text{H}^5)^4.\text{I}$  = iodethylate of triethylamine  $\text{N}(\text{C}^2\text{H}^5)^3.\text{C}^2\text{H}^5.\text{I}$ . They are, in fact, produced by the direct combination of ethyl-salts with triethylamine; but their chemical reactions are most simply represented by regarding them as ammonium- not as ammonia-salts.

There are likewise ethyl-bases containing methyl, amyl, phenyl, &c., as well as ethyl.

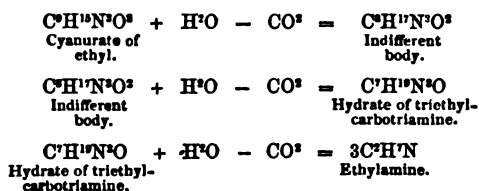


Compt. rend. xxviii. 223 and 323; Ann. Ch. Phys. [3] xxx. 443.)

*Formation.*—1. By the action of potash on cyanate or cyanurate of ethyl (Wurtz):

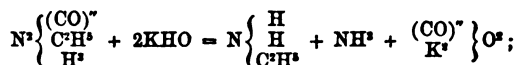


In the case of cyanuric ether, however, the transformation into ethylamine does not take place at once, as the preceding equation would indicate; but by three successive steps, each consisting in the assimilation of a molecule of water and the elimination of a molecule of carbonic anhydride, the intermediate products being an indifferent oily body, first observed by Habich and Lämprecht (*p. 293*), and hydrate of triethyl-carbotriamine:



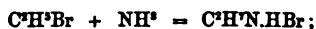
The same products are sometimes obtained by the action of ethylate of sodium on cyanurate of ethyl, and sometimes on the cyanate. (Hofmann, Proc. Roy. Soc. xi. 284.)

2. By the action of potash on ethyl-carbamide (ethyl-urea) (Wurtz):



and similarly according to Tuttle (Ann. Ch. Pharm. ci. 288), by distilling a mixture of urea, ethylsulphate of calcium, and caustic lime, or a mixture of cyanate of potassium, ethylsulphate of calcium, and slaked lime.

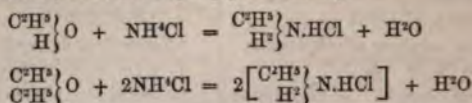
3. By the action of ammonia on various ethylic ethers, *viz.* on the bromide or iodide (Wurtz; Hofmann, Chem. Soc. Qu. J. iii. 300):



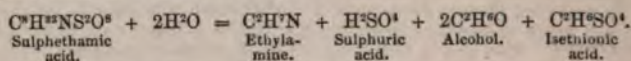
on the chloride (Groves, Chem. Soc. Qu. J. xiii. 331), phosphate (De Clermont,

Ann. Ch. Phys. [3] xlv. 335), nitrate (Juncadella, Compt. rend. xlviii. 332), or sulphite (Carius, Ann. Ch. Pharm. cx. 209).

4. By heating chloride, bromide, or iodide of ammonium with alcohol or ether in sealed tubes (Berthelot, Ann. Ch. Phys. [3] xxxviii. 63):



5. By the decomposition of sulphethamic acid, that compound being resolved by heat into ethylamine, sulphuric acid, and probably alcohol and isethionic acid. (Strecker, Ann. Ch. Pharm. lxxv. 50.)



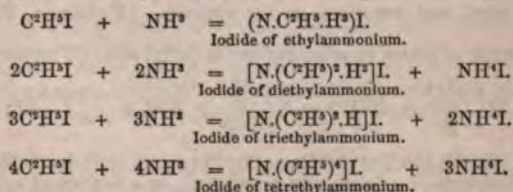
6. Cyanide of ethyl left in contact for some time with hydrochloric or sulphuric acid, yields a salt of ethylamine, just as cyanide of hydrogen treated in the same manner yields a salt of ammonia. (E. Meyer, J. pr. Chem. lxxviii. 279.)

7. White precipitate ( $\text{NH}^2\text{Hg}^2\text{Cl}$ ) heated with iodide of ethyl forms a double chloride of mercury and ethylammonium, a corresponding double iodide, and other compounds (p. 535).

*Preparation.*—1. By decomposing cyanate of ethyl with potash. The action takes place at ordinary temperatures, and is attended with great evolution of heat; hence it is best to mix the liquids in a bottle having a well ground stopper, which must be tightly secured, and to cool the bottle externally. The decomposition is complete in about five minutes, the vessel then containing nothing but ethylamine and carbonate of potassium. The liquid is then distilled, and the vapour of ethylamine passed into a receiver containing a little water, and cooled externally. To obtain the anhydrous base, the aqueous solution thus formed is saturated with hydrochloric acid; and the hydrochlorate of ethylamine crystallised by evaporation, thoroughly dried, and gently heated with twice its weight of quick lime in a long glass tube, closed at one end, the mixture occupying the lower half of the tube, while the upper half is filled with fragments of caustic potash to dry the vapour of ethylamine as it is evolved. The dry vapour then passes through a delivery-tube into a small flask or U-tube surrounded with a freezing mixture, and is there condensed to a liquid. (Wurtz.)

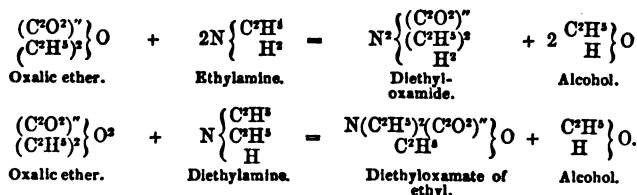
2. By the action of ammonia on bromide of ethyl. Strong ammonia is enclosed, together with excess of bromide of ethyl, in a combustion-tube two feet long, and the sealed tube is immersed in boiling water. Decomposition takes place quickly, with ebullition, and is complete in about a quarter of an hour, its completion being indicated by the volume of the bromide of ethyl remaining constant instead of diminishing. The tube then contains hydrobromate of ethylamine, from which the base may be obtained by distillation with potash or lime. (Hofmann, Chem. Soc. Qu. J. iii. 300.)

3. By heating iodide of ethyl with ammonia in sealed tubes. The action in this case is more complicated than when the bromide is used, the formation of iodide of ethylammonium being accompanied by that of iodide of ammonium, and of the iodides of di-, tri-, and tetrethylammonium, as shown by the following equations:

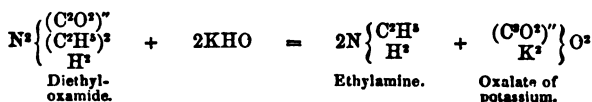


This mixture of iodides distilled with potash, yields a distillate consisting of ammonia, ethylamine, diethylamine and triethylamine (the hydrate of tetrethylammonium formed at the same time being resolved into triethylamine, water, and ethylene (p. 561), which it is impossible to separate completely by fractional distillation. The separation may however be effected by subjecting the mixture of bases previously dehydrated, to action of *oxalate of ethyl*, by which the ethylamine is converted into diethyloxaz-

mide, and the diethylamine into diethyloxamate of ethyl, while the triethylamine remains unaltered:



On distilling the product of this reaction at the heat of the water-bath, the triethylamine, which has not been acted on, passes over pure. The residue consists of a fibrous mass of diethyloxamide saturated with an oily liquid, which is diethyloxamate of ethyl. On submitting this mixture to the action of boiling water, the diethyloxamide dissolves, and the diethyloxamate of ethyl remains as an insoluble oily layer floating on the hot solution, from which it may be separated by a tap-funnel. The diethyloxamide crystallises from the aqueous solution on cooling, and when distilled with potash, yields pure ethylamine:



The oily liquid serves for the preparation of diethylamine, p. 559. (Hofmann, Proc. Roy. Soc. xi. 66, 526.)

4. From nitrate of ethyl. Nitric ether is mixed with twice or three times its weight of absolute alcohol previously saturated with ammoniacal gas; the mixture is heated to 100° C. for two days in a sealed tube half filled with it, then distilled with excess of potash; the vapours which pass over are received in hydrochloric acid; and the chloride of ethyl-ammonium thus formed is separated from chloride of ammonium by solution in alcohol (Juncadella). According to Carey Lea, nitrate of ethyl heated with ammonia yields diethylamine and a small quantity of triethylamine, as well as ethylamine. To separate these bases, he distils the contents of the tube with potash; receives the vapours in dilute sulphuric acid; dissolves out the sulphates of the ethyl-bases with alcohol, which leaves sulphate of ammonium undissolved; then converts them into picrates; and separates the picrates of ethylamine and diethylamine by repeated crystallisation, the ethylamine-salt being the less soluble of the two. The quantity of triethylamine produced is too small to interfere with the process, unless the reaction is conducted in a particular manner to be afterwards described (p. 559). The picrates of ethylamine and diethylamine are decomposed by hydrochloric acid, and the bases are obtained by distillation with potash. (Chemical News, v. 118; Rép. Chim. pure, 1862, p. 239.)

*Properties.*—Anhydrous ethylamine is a transparent, colourless, very mobile, inflammable liquid, of specific gravity 0.6964 at 8° C. It does not solidify at the temperature of a mixture of solid carbonic acid and ether. Boils at 18.7° C. (Wurtz). Vapour density at 43° and under a pressure of 773.04 mm. = 1.5767 (Izarn). It has a very pungent ammoniacal odour, a strong alkaline reaction, and is highly caustic, a small drop of the concentrated aqueous solution placed upon the tongue producing a burning pain and acute inflammation. It forms very dense white fumes with hydrochloric acid gas, and makes a hissing noise when strong hydrochloric acid is dropt into it. (Wurtz.)

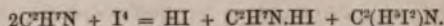
Ethylamine mixes with water in all proportions, the mixture being attended with considerable rise of temperature. The solution is distinguished from aqueous ammonia by a certain degree of viscosity. By continued boiling, the whole of the ethylamine may be expelled.

The solution of ethylamine exhibits, with many metallic salts, reactions similar to those of ammonia. It is however distinguished from ammonia by redissolving the precipitates which it forms with solutions of *aluminium* (Wurtz), *gold*, and *ruthenium* (Carey Lea), and by not redissolving those which it forms with salts of *cadmium*, *nickel*, and *cobalt*. The precipitate formed with *cupric salts* is less easily soluble in ethylamine than in ammonia (Wurtz). With *stannic chloride*, ethylamine forms a precipitate very soluble in excess, whereas that formed by ammonia dissolves but slowly in excess of that alkali. The precipitate formed by ethylamine in *gold-salts* has but little resemblance to fulminating gold: it is decomposed by heat, but without



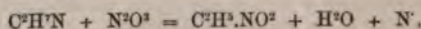
detonation (Carey Lea). *Dichloride of platinum* is not immediately precipitated by ethylamine from a moderately concentrated solution (Wurtz). *Phosphomolybdic acid* forms, with solution of ethylamine, a yellow precipitate like that with ammonia, but more soluble (Meyer).

*Decompositions*.—1. Ethylamine vapour passed through a red-hot porcelain tube is resolved into ammonia, hydrocyanic acid, hydrogen, and a small quantity of a hydrocarbon.—2. On the approach of a burning body, it takes fire and burns with a yellowish flame.—3. *Iodine* decomposes the aqueous solution of ethylamine, forming hydriodate of ethylamine and diiodoethylamine, which cannot be distilled without decomposition:



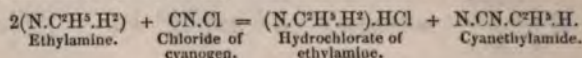
*Bromine and chlorine* act in like manner.

4. *Nitrous acid* decomposes ethylamine, with formation of nitrous ether and free nitrogen:

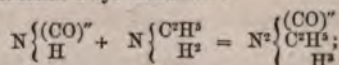


An easy way of exhibiting this reaction is to drop a crystal of nitrite of potassium into a solution of hydrochlorate of ethylamine, mixed with an equal volume of hydrochloric acid. A small quantity of yellow aromatic oil is formed at the same time.

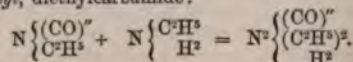
5. With *chloride of cyanogen*, ethylamine acts like ammonia; thus:



6. With *cyanic acid* it forms ethyl-carbamide:



and with *cyanate of ethyl*, diethylcarbamide:



7. *Oil of mustard* (sulphocyanate of allyl) converts ethylamine into thiosinethylamine,  $\text{C}^2\text{H}^5\text{N}^2\text{S}$ . (Hinterberger, Ann. Ch. Pharm. lxxxiii. 346.)

8. For the reaction of ethylamine with *dibromide of ethylene*, see **ETHYLENE-BASES**.

**Salts of Ethylamine.** Ethylamine is a strong base, neutralising acids as completely as ammonia, and expelling ammonia from ammoniacal salts. Most salts of ethylamine are easily soluble in alcohol, a property by which they are distinguished from salts of ammonia. Hence, when the two bases occur together, they may be separated by converting them into chlorides or sulphates, and digesting the dried residue in strong alcohol. According to Meyer (J. pr. Chem. lxvii. 147), the separation is easily effected by treating the mixed bases with excess of tartaric acid, and evaporating; acid tartrate of ammonium then crystallises out, while the ethylamine-salt remains in the form of a syrup, easily soluble in alcohol.

*Acetate of Ethylamine.*—When ethylamine vapour is passed into a vessel containing glacial acetic acid and surrounded with ice, the salt is obtained in the form of a very deliquescent, crystalline mass of dazzling whiteness. Phosphoric anhydride chars it rapidly, but does not give rise to the formation of any compound analogous to acetonitrile. (Wurtz.)

*Bromhydrate or Hydrobromate of Ethylamine*,  $\text{C}^2\text{H}^5\text{N.HBr}$ , or *Bromide of Ethylammonium*,  $\text{C}^2\text{H}^5\text{N.Br}$ .—This salt is produced: 1. By the direct combination of ethylamine and hydrobromic acid.—2. By the action of bromine on aqueous ethylamine (Wurtz).—3. By the action of bromide of ammonium on alcohol or ether (Berthelot, p. 553).—4. By the action of ammonia on bromide of ethyl. It is crystalline, and gives off ammonia when distilled with potash.

*Carbonate of Ethylamine.*—When hydrochlorate of ethylamine is carefully distilled with carbonate of sodium, both being thoroughly dry, carbonate of ethylamine passes over, and condenses as a crystalline mass saturated with a viscid liquid, whose solution has a strong alkaline reaction. It has an ammoniacal odour, gives off, even at ordinary temperatures, vapours which turn reddened litmus blue; is very deliquescent, and dissolves the basic carbonates of copper and zinc. The analysis of this salt yielded quantities of carbon and hydrogen greater than are required by the formula of acid carbonate of ethylamine,  $\text{C}^2\text{H}^5\text{N.H.CO}^2$ .

Respecting the so-called *anhydrous carbonate of ethylamine*, obtained by passing carbonic anhydride into anhydrous ethylamine, see below.

*Chlorhydrate or Hydrochlorate of Ethylamine*,  $C^2H^5N.HCl$ , or *Chloride of Ethylammonium*,  $C^2H^5N.Cl$ .—Formation similar to that of the hydrobromate. Prepared by saturating with hydrochloric acid the aqueous solution of ethylamine, which is obtained by distilling cyanic acid with potash. On evaporating to dryness, dissolving the residue in strong boiling alcohol, and cooling the solution, the salt is deposited in large crystalline laminae. From the aqueous solution it crystallises in striated prisms. Fuses between  $76^\circ$  and  $80^\circ$  C., and solidifies on cooling in a semi-transparent, crystalline mass. Gives off vapours at a high temperature; boils between  $315^\circ$  and  $320^\circ$ ; and if then left to cool, solidifies in a milk-white, amorphous mass, whose melting point is above  $260^\circ$ . The crystals are very deliquescent. On treating the aqueous solution with amalgam of potassium, hydrogen is given off and a solution of ethylamine is formed. (Wurtz.)

*Chloro-aurate*,  $C^2H^5NCl.AuCl^3$ .—Obtained by mixing the aqueous solutions of hydrochlorate of ethylamine and trichloride of gold. Forms very fine, golden-yellow, prismatic crystals, soluble in water, alcohol, and ether. (Wurtz.)

*Chloromercurate*,  $C^2H^5NCl.HgCl$ , or  $(C^2H^5NCl)^2.Hg^2Cl^2$ .—Obtained by mixing the aqueous solutions of corrosive sublimate and hydrochlorate of ethylamine in equivalent quantities. Crystallises more readily than the corresponding salt of methylamine, but forms smaller crystals. From the alcoholic solution it is deposited in small white scales. (Wurtz.)

*Chloride of Ethylammonium with Cyanide of Mercury*,  $C^2H^5NCl.Hg^2Cy^2$ .—Obtained by mixing a neutral solution of hydrochlorate of ethylamine with aqueous cyanide of mercury, and evaporating over the water-bath to the crystallising point. Large laminated crystals, which are permanent in the air, and are decomposed by the heat of the water-bath. Soluble in water, sparingly in cold alcohol. Taste disagreeably metallic. (Kohl and Swoboda, Ann. Ch. Pharm. lxxxiii. 342.)

*Chloropalladite of Ethylamine*,  $C^2H^5NCl.PdCl$ .—An aqueous solution of hydrochlorate of ethylamine evaporated over the water-bath with excess of protochloride of palladium, yields large black crystals grouped in feathery tufts; by transmitted light they exhibit a fine red colour. They yield a red-brown powder, and retain their lustre unimpaired at the heat of the water-bath. (Reckenschuss, Ann. Ch. Pharm. lxxxiii. 343.)

*Chloroplatinate*,  $C^2H^5NCl.PtCl^2$ .—Obtained by mixing the concentrated solutions of dichloride of platinum and chloride of ethylammonium, adding alcohol, pressing the resulting yellow precipitate, and dissolving it in boiling water. On cooling, the double salt separates in beautiful tablets of a deep orange-yellow colour. (Wurtz.)

For the compounds of ethylamine with protochloride of platinum and other platinous salts, see PLATINUM-BASES.

*Ethylcarbamate of Ethylammonium*,  $C^2H^5N^2O^2 = \frac{NH(C^2H^5)(CO)^2}{C^2H^5N} \bigg\} O = (C^2H^5N)^2.CO^2$ .—This salt, homologous with the so-called *anhydrous carbonate of ammonia*, is produced by passing carbonic anhydride into anhydrous ethylamine cooled by a freezing mixture (i. 761).

*Molybdate of Ethylamine*,  $(C^2H^5N)^2.H^2Mo^6O^7 = (C^2H^5N)^4.Mo^6O^7$ .—Molybdic acid dissolves readily in ethylamine, and the solution left to evaporate over chloride of calcium deposits white scales, which become red-brown when dry, and ultimately assume a regular brown colour. They continually give off ethylamine, and are gradually converted into a more acid salt. (Meyer, J. pr. Chem. lxvii. 161.)

*Nitrate of Ethylamine*.—Obtained by saturating ethylamine with nitric acid. Very deliquescent; crystallises from the aqueous solution in thin laminae. The syrupy mother-liquor, when heated, gives off gases which burn with a yellow flame, and yields a brown watery distillate with a few drops of oil floating on the surface; the residue is a brown mass which ultimately becomes charred. (Wurtz.)

*Oxalate of Ethylamine*,  $(C^2H^5N)^2.H^2C^2O^4 = \frac{(C^2O^2)^2}{(C^2H^5N)^2} \bigg\} O^2$ .—Obtained by saturating ethylamine with oxalic acid and evaporating. Crystallises in right rhombic prisms. When heated it gives off 2 at. water, and is converted into ethyloxamide,  $N^2.(C^2O^2)^2.(C^2H^5)^2.H^2$ . Heated with excess of oxalic acid, it yields a small quantity of ethyloxamic acid. (See OXAMIC ACID.)

*Phosphate of Ethylammonium and Magnesium*,  $C^2H^5N.Mg.H.PO^4 + 5H^2O$ ? Obtained by adding ordinary phosphate of sodium to a solution of sulphate of magnesium mixed with ethylamine and either of its salts, as a bulky precipitate which becomes crystalline on standing, is much more soluble than the corresponding ammo-

nium-salt; and when left over sulphuric acid, gives off all its water and part of the ethylamine. (Meyer.)

*Sulphate of Ethylamine* or of *Ethylammonium*.—Deliquescent, uncrystallisable, very soluble in alcohol, dries up in vacuo to a transparent gummy mass. (Wurtz.)

*Sulphate of Ethylammonium and Aluminium*. *Ethylamine-alum*.  $\left\{ \begin{smallmatrix} \text{C}^2\text{H}^5\text{N} \\ (\text{Al}^3)^3 \end{smallmatrix} \right\} 2\text{SO}^4 + 12\text{H}^2\text{O}$ .—Obtained by mixing the solutions of the component salts, and evaporating. Crystallises ordinarily in regular octahedrons like common alum, but occasionally in prisms, which, however, yield octahedrons by recrystallisation. (Kenner and Stammer, Ann. Ch. Pharm. xci. 172; Meyer, *loc. cit.*)

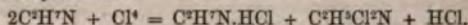
Sulphate of ethylamine also forms crystallisable double salts with the *sulphates of magnesium and copper*, and with *chloride of copper* (Meyer); with *sulphate of zinc*. (Carey Lea.) The magnesium-salt appears to contain  $\text{C}^2\text{H}^5\text{N}.\text{Mg}.\text{SO}^4 + \frac{1}{2} \text{ aq.}$  (Meyer.)

*Sulphhydrate of Ethylammonium*. Prepared by passing sulphydric acid gas into anhydrous ethylamine cooled with ice. Colourless, easily fusible, volatile crystals, which, when exposed to the air, absorb moisture, and change to yellow drops. (Wurtz.)

*Tartrate of Ethylammonium and Sodium* has been obtained by Carey Lea.

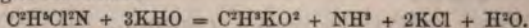
#### Substitution-products of Ethylamine.

**DICHLORETHYLAMINE.**  $\text{C}^2\text{H}^5\text{Cl}^2\text{N}$ . (Wurtz, Ann. Ch. Phys. [3] xxx. 474.)—Chlorine passed into aqueous ethylamine cooled with ice, forms this compound, together with hydrochlorate of ethylamine:



The action is attended with rise of temperature and a slight evolution of nitrogen gas. The dichlorethylamine is deposited in the form of a yellow liquid, which may be purified by washing with water and rectifying over chloride of calcium. It has a penetrating odour, and produces coughing and flow of tears. Boils at  $91^\circ \text{C}$ . The vapour explodes when heated in a tube, but not with sufficient force to break the tube.

The compound treated with excess of chlorine is converted into a solid body which crystallises in scales. Ammonia decomposes and dissolves it gradually. Caustic potash decomposes it slowly, forming chloride of potassium, acetate of potassium, and ammonia, a gas containing chlorine being also given off in small quantity, and a few drops of an oily liquid, which has a disagreeable odour, like that of impure cyanide of ethyl, sinking to the bottom:



The gas and the oily liquid are secondary products. (Wurtz.)

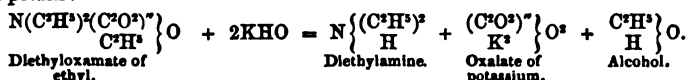
**DIBROMETHYLAMINE.**  $\text{C}^2\text{H}^5\text{Br}^2\text{N}$ . (Wurtz, Ann. Ch. Phys. [3] xxx. 477.)—Bromine acts on ethylamine in the same manner as chlorine, and with considerable violence, so that it is necessary to add the bromine drop by drop, and cool the liquid with ice. The greater part of the resulting dibromethylamine remains dissolved in the watery liquid, only a small portion settling down in the form of an oil as the action approaches its termination. The dissolved portion may, however, be extracted by agitating with ether, and evaporating the ethereal solution. The product is an oily liquid having an orange-red colour arising from a slight excess of bromine, which may, however, be removed by agitation with weak potash. It is heavier than water, and has a pungent odour.

**DINIODETHYLAMINE.**  $\text{C}^2\text{H}^5\text{I}^2\text{N}$ . (Wurtz, Ann. Ch. Phys. [3] xxx. 478.)—Iodine introduced into an aqueous solution of ethylamine exerts an immediate action, attended with rise of temperature, producing hydriodate of ethylamine, and a bluish black liquid which is diniodeethylamine. This compound decomposes when distilled, giving off vapours of iodine, and consequently has not yet been obtained in a state of purity. It is soluble in alcohol and ether. Caustic potash decomposes it gradually, forming iodide of potassium, a small quantity of iodate, and a yellow crystalline residue, the composition of which has not been ascertained.

**Diethylamine.**  $\text{C}^4\text{H}^{11}\text{N} = \text{N} \left\{ \begin{smallmatrix} (\text{C}^2\text{H}^5)^2 \\ \text{H} \end{smallmatrix} \right\}$ . (A. W. Hofmann, Phil. Trans. 1850, p. 120; Chem. Soc. Qu. J. iii. 300.)—This compound is produced: 1. As hydrobromate by heating an aqueous solution of ethylamine with bromide of ethyl in sealed tubes ( $\text{C}^2\text{H}^5\text{N} + \text{C}^2\text{H}^5\text{Br} = \text{C}^4\text{H}^{11}\text{N}.\text{HBr}$ ), and may be obtained in the free state by dis-



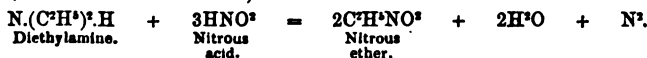
tillation with potash.—2. As a hydriodate, together with the corresponding compounds of the other ethyl-bases, by heating iodide of ethyl with ammonia in sealed tubes, and may be separated by Hofmann's method already described. The liquid diethyloxamate of ethyl is separated from the crystalline diethyloxamide by the method described on page 555, and then distilled. The boiling point quickly rises to 260° C., and the liquid which passes over at that temperature yields diethylamine by distillation with potash:



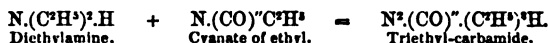
3. Nitrate of ethyl heated with ammonia yields a mixture of ethylamine and diethylamine, which may be separated in the manner described on pp. 555, 560. (Carey Lea.)

Diethylamine is a volatile, inflammable liquid, boiling at 57° C., very soluble in water, and having a strong alkaline reaction (Hofmann). With *metallic salts*, it acts for the most part like ethylamine, but it is distinguished therefrom by three reactions: 1. It does not precipitate a solution of *protochloride of palladium*.—2. The precipitate which it forms with *sino-salts* is not soluble in excess of diethylamine.—3. Added in large excess to a solution of *mercuric chloride*, it forms a precipitate which is not soluble in acetic acid, whereas the precipitates formed in like manner by ethylamine and by ammonia, dissolve easily in that acid. (Carey Lea.)

*Iodine* acts on diethylamine in the same manner as on ethylamine, forming an oily substitution-product. *Nitrous acid* acts upon it in the same manner as on ethylamine. (Riche, Ann. Ch. Pharm. cxi. 91.)



With *cyanate of ethyl* it forms triethylcarbamide (Hofmann, Compt. rend. liv. 252).



For the reaction of diethylamine with *dibromide of ethylene*, see ETHYLENE-BASES.

The salts of diethylamine are not much known. The *chloroplatinate*,  $\text{C}^2\text{H}^5\text{N} \cdot \text{Cl} \cdot \text{PtCl}_2$ , is moderately soluble, and crystallises in orange-red granules (Hofmann). Wetzien obtained large orange-yellow shining crystals, which, according to J. Müller, belong to the monoclinic system.

**Triethylamine.**  $\text{C}^2\text{H}^5\text{N} = \text{N}(\text{C}^2\text{H}^5)^3$ . (Hofmann, *loc. cit.*—Carey Lea, Chemical News, vi. 142; Rép. Chim. pure, 1862, p. 446.)—Produced: 1. By heating diethylamine with bromide of ethyl, and distilling the resulting bromide of triethylammonium with potash.

2. By the action of ethylate of potassium or sodium on cyanate of ethyl, precisely as ethylamine is produced from hydrate of potassium and cyanic ether:



The materials are digested together for several hours at a moderate heat, and then distilled in a sand-bath. The strongly alkaline distillate, saturated with hydrochloric acid and evaporated, yields a residue from which pure triethylamine may be obtained by distillation with potash. The cyanic ether and the sodium-alcohol must be perfectly anhydrous, otherwise the chief product of the reaction will be ethylamine; but even when water is altogether absent, a different reaction sometimes takes place, attended with the formation of triethylcarbatriamine (p. 560).

3. Iodide of triethylammonium is obtained, together with other iodides, by heating iodide of ethyl in a sealed tube with ammonia. The product distilled with potash yields a mixture of ethylamine, diethylamine, and triethylamine, which may be separated by means of oxalic ether as described at p. 555. The triethylamine not being acted upon, passes over by simple distillation. (Hofmann.)

4. Nitrate of ethyl heated in sealed tubes with ammonia always yields a certain quantity of triethylamine, together with ethylamine and diethylamine, and, by proceeding as follows, the proportion of triethylamine may be considerably increased. A mixture of 3 volumes nitrate of ethyl, 3 volumes strong aqueous ammonia, and 2 volumes absolute alcohol, is heated to 100° C. in a sealed tube for four hours. The contents of the tube are then exactly saturated with nitric acid, and evaporated over the water-bath; the pasty mass is dissolved in 4 volumes of absolute alcohol; the solution is distilled with a considerable excess of caustic soda; the distillate is received in a mixture of 3 volumes nitrate of ethyl and 2 volumes absolute alcohol surrounded

by a freezing mixture; and the liquid thus saturated with the alkaline vapour is introduced into sealed tubes and heated in a water-bath. This mode of proceeding yields a product in which the proportion of ethylamine is very small, and of the remainder the diethylamine constitutes three-fourths, the triethylamine one-fourth. To separate these bases, they are converted into picrates, the picrates of ethylamine and triethylamine crystallising out in needles, and the picrate of diethylamine afterwards separating as a heavy oil. The crystalline picrates of the two bases are distilled with an alkali; the vapours condensed in water, and the solution, after moderate concentration, is agitated with ten times its volume of ether, which takes up the triethylamine, leaving the ethylamine dissolved in the water. (Carey Lea.)

5. Triethylamine is given off, together with ethylene and water, in the decomposition of hydrate of tetrethylammonium by heat. (Hofmann.)

Triethylamine is a colourless, strongly alkaline liquid, inflammable, having an agreeable ammoniacal odour; it is but sparingly soluble in water, and, when the quantity of water present is not sufficient to dissolve it, floats on that liquid like an oil. (Hofmann; Lea.)

The aqueous solution forms with salts of *zirconium*, *glucinum*, *cadmium*, and *zinc*, white precipitates insoluble in excess; with *aluminium*-salts, a precipitate easily soluble in excess. It forms a green precipitate with *nickel* salts, greenish-blue with *cobalt* salts, white with *stannous* salts, brown with *nitrate of silver*, reddish-brown with *pentachloride of antimony*, yellow with *uranic* salts, yellowish-white with salts of *mercury*, greyish with salts of *iron*, blue with *copper* salts, white with salts of *magnesium* and *cerium*,—all these precipitates being insoluble in excess of the alkali. With *stannic chloride* it forms a precipitate soluble in excess of the alkali; with *acetate of lead*, a precipitate insoluble in excess of the alkali, but soluble in excess of the lead salt. It does not precipitate the salts of *platinum* or *palladium*. With *trichloride of gold*, it forms a yellow precipitate insoluble in excess, and blackening rapidly, from formation of protoxide of gold, the reduction being attended with evolution of aldehyde. This is the most characteristic reaction of triethylamine. (Carey Lea.)

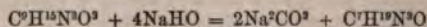
*Hydrobromate of Triethylamine* or *Bromide of Triethylammonium* crystallises in beautiful fibrous crystals several inches long. (Hofmann.)

The *hydrochlorate* crystallises in white laminae; it is not deliquescent, very inflammable, volatilises easily without decomposition. (Carey Lea.)

The *chloroplatinate*,  $C^3H^9NCl.PtCl_2$ , is very soluble in water, and crystallises on cooling from strong solutions in splendid orange-red rhombic crystals. (Hofmann.)

The *nitrate* does not crystallise, but remains in the form of a thick syrup, when its solution is evaporated in vacuo. The *sulphate* is very soluble in water and alcohol; by evaporation in vacuo it is obtained as a confused crystalline mass. It forms a double salt with sulphate of zinc. (Carey Lea.)

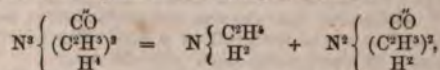
**Triethylcarbottriamine**,  $C^3H^{11}N^3 = N^3\{C^{'''H^3}(C^2H^3)^3H^2\}$ ; or **Triethyleyano-diamine**,  $N^2\{CN.(C^2H^3)^3.H^2\}$ . (Hofmann, Proc. Roy. Soc. xi. 282.)—Not known in the separate state, but obtained as a hydrate,  $C^3H^{11}N^3O = C^3H^{11}N^3.H^2O$ , by heating ethylate of sodium with cyanurate of ethyl (sometimes also with the cyanate), the ethylate of sodium being then resolved by the heat into ethylene,  $C^2H^4$ , which escapes, and hydrate of sodium, which acts on the cyanuric ether in the manner represented by the equation:



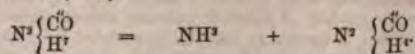
The reaction actually takes place by several stages, as already explained (p. 553).

Hydrate of triethylcarbottriamine is a basic oil, which neutralises acids, forming definite salts. The *gold-salt*,  $C^3H^{11}N^3.HCl.AuCl^3$  and the *platinum-salt*,  $C^3H^{11}N^3.HCl.PtCl^2$  have been analysed. The iodide forms splendid crystals.

The hydrated base, which may also be regarded as *triethyl-carbonyl-triamine*, is resolved by distillation into ethylamine and diethylcarbamide:



just as guanidine (carbonyl-triamine) is resolved, under certain circumstances, into ammonia and carbamide (urea):



**Diethylamylamine**,  $C^3H^9N = N(C^2H^3)^2.C^3H^9$  (Hofmann, Chem. Soc. Qu. J. iv. 315).—Obtained together with water and ethylene-gas by the dry distillation of hydrate of triethylamylammonium (p. 563). It is an oily liquid, heavier than water,

bitter, and having a not unpleasant odour. Boils at  $154^{\circ}\text{C}$ . Soluble in water. The *sulphate*, *hydrochlorate*, *nitrate*, and *oxalate* crystallise easily but are deliquescent. The *chloroplatinate* crystallises in orange-yellow needles of extraordinary beauty.

**Tetrethylammonium.**  $\text{C}^4\text{H}^{10}\text{N} = \text{N}(\text{C}^2\text{H}^5)^4$ . *Tetrethylum*. (Hofmann, Phil. Trans. 1861, p. 357; Chem. Soc. Qu. J. iv. 304.)—This compound, which, like ammonium itself, is not known in the free state, is obtained as an iodide or bromide by the action of iodide or bromide of ethyl on triethylamine:



Iodide of ethyl acts quickly with the aid of heat, the bromide slowly.

The iodide or bromide treated with moist oxide of silver, yields a strongly alkaline solution, containing the hydrate of tetrethylammonium, and this, when treated with acids, yields the other salts. The bromide, chloride, iodide, carbonate, nitrate, phosphate, and sulphate are all crystalline. The orthophosphate  $(\text{C}^4\text{H}^{10}\text{N})^4\text{PO}_4$ , is strongly alkaline.

*Bromide of Tetrethylammonium* forms white opaque granular crystals. (Hofmann.)

The *chloride*, obtained by neutralising the solution of the hydrate with hydrochloric acid, forms double salts with the chlorides of gold, mercury, and platinum.

*Chloro-aurate.*  $\text{C}^4\text{H}^{10}\text{NCl}_2\text{AuCl}_2$ .—Lemon-yellow precipitate obtained by mixing the solutions of the two chlorides. Dissolves but sparingly in cold water and in hydrochloric acid.

*Chloromercurates.*—*a.*  $\text{C}^4\text{H}^{10}\text{NCl}_2\text{HgCl}$ . White crystalline precipitate, soluble in water and in hydrochloric acid, especially at the boiling heat. From the boiling solution it separates in plates having an unctuous appearance. (Hofmann.)

*b.*  $\text{C}^4\text{H}^{10}\text{NCl}_2\text{HgCl}$ .—Obtained by decomposing the yellow crystals  $\text{C}^4\text{H}^{10}\text{N}^+\text{Hg}^+\text{I}^-$  (pp. 638, 665), with oxide of silver, neutralising the resulting alkaline liquid with hydrochloric acid, and evaporating. It forms white crystals. (Sonnenschein.)

*Chloroplatinate.*  $\text{C}^4\text{H}^{10}\text{NCl}_2\text{PtCl}_2$ .—Dichloride of platinum added to chloride of tetrethylammonium, immediately forms an orange-yellow precipitate, resembling the corresponding potassium and ammonium-salts. Slightly soluble in water; less soluble in alcohol and ether. May be crystallised in beautiful octahedrons. (Hofmann.)

*Hydrate.*  $\text{C}^4\text{H}^{10}\text{NO} = \text{N}(\text{C}^2\text{H}^5)^4\text{O}$ .—Prepared by decomposing the iodide with oxide of silver. The solution of the iodide is gently heated, and recently precipitated oxide of silver added in small portions with agitation, till the resulting iodide of silver assumes a permanent yellow colour. The liquid filtered from the silver-precipitate is a solution of the hydrate of tetrethylammonium. It may likewise be obtained by decomposing the sulphate with baryta; but this process is not so good as the preceding, on account of the difficulty of getting rid of the excess of baryta or of sulphuric acid. The alkaline solution, evaporated in vacuo over sulphuric acid and lime yields, after some time, long hair-like needles which are extremely deliquescent and attract carbonic acid rapidly from the air. By remaining longer in vacuo, the crystals disappear again, and the liquid dries up to a semi-solid mass, which also deliquesces and attracts carbonic acid rapidly.

The solution of this compound is strongly alkaline, and has the pungent bitterness of quinine. In the concentrated state, it burns the tongue and acts on the epidermis like caustic potash or soda; rubbed between the fingers, it excites the well-known sensation produced by the fixed alkalis, and the same peculiar odour. It saponifies fats as readily as potash, converts furfuramide into furfurine, and decomposes oxalic ether into oxalic acid and alcohol. With metallic solutions it behaves like caustic potash, excepting that hydrate of alumina is less soluble in it, and hydrated chromic oxide quite insoluble.

A moderately concentrated solution of hydrate of tetrethylammonium may be boiled without alteration, but at an advanced state of the evaporation, decomposition sets in, even at the temperature of the water-bath, the residue intumescing strongly, and being gradually but completely resolved into water, triethylamine and olefant gas:



The solution of the hydrate boiled for about 24 hours with iodide of ethyl in a flask provided with a condensing tube, so that the volatilised products may be condensed and run back, becomes perfectly neutral, and is converted into alcohol and iodide of tetrethylammonium:





A concentrated solution of the hydrate mixed with an alkaline solution of iodide of potassium, yields a crystalline precipitate of iodide of tetrethylammonium; this effect is due to the insolubility of the latter substance in alkaline liquids.

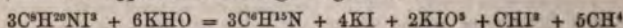
*Iodides of Tetrethylammonium.*—*a. Protiodide.*  $C^8H^{20}NI$ . When perfectly anhydrous iodide of ethyl is added to triethylamine, dried over hydrate of potassium, the mixture becomes slightly turbid, heat being evolved at the same time. The action goes on but slowly at ordinary temperatures, the mixture, after several days, being converted into a solid mass; but on exposing the mixture for a minute or two to the temperature of boiling water, a powerful reaction ensues, the liquid remaining for some time in a state of brisk ebullition, even after removal of the heat, and solidifying on cooling, into a hard mass of crystals, which is snow-white or yellowish, according as the triethylamine or the iodide of ethyl is in excess. To avoid loss of triethylamine, it is best to heat the mixture in sealed tubes. On dissolving the crystalline mass in cold water and leaving the solution to evaporate spontaneously, the iodide is obtained in beautiful, well-defined, white crystals, of considerable size, which may be separated by mechanical means from small quantities of a reddish iodine-compound sometimes formed by the action of the air. This latter substance is formed in much larger quantity at higher temperatures, for which reason it is best to avoid the use of hot water in the purification (*vid. infra*).

The crystals are anhydrous, and do not diminish in weight by exposure to the temperature of boiling water. When rapidly heated to a higher temperature, they fuse, and are decomposed into triethylamine and iodide of ethyl, which form two layers in the receiver, but quickly unite and reproduce the original compound.

The aqueous solution mixed with caustic potash solidifies at once to a crystalline mass consisting of the iodide itself, which is less soluble in alkaline liquids than in pure water. With nitrate or sulphate of silver, it yields iodide of silver, and a solution of nitrate or sulphate of tetrethylammonium. With oxide of silver it yields a solution of the hydrated oxide of tetrethylammonium.

*b. Teriodide.* When iodide of ethyl is heated for some time with alcoholic ammonia in such a manner that the volatilised portions may condense and run back again, a liquid is formed containing iodide of ammonium, and the iodides of the four ethylammoniums; and this liquid, when exposed to the air for about a month (whereby the iodide of ammonium is decomposed and iodine set free), yields teriodide of tetrethylammonium in large, shining, dark-red, prismatic crystals. The same compound is more quickly obtained by heating the liquid with iodine; it then separates in small needle-shaped crystals. (Weltzien, Ann. Ch. Pharm. lxxxvi. 292; xli. 33.)

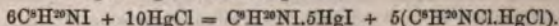
Teriodide of tetrethylammonium boiled with aqueous potash is partially decomposed, giving off a volatile ethyl-base, probably triethylamine, and forming iodide of potassium, iodate of potassium, and iodoform. To account for the formation of these products, however, we must suppose that marsh gas is given off:



Teriodide of tetrethylammonium dissolves slowly in cold water, readily in boiling alcohol; from the latter solution it crystallises in needles arranged in feathery groups. It dissolves in the iodides of potassium, sodium, and the ethyl-ammoniums, and separates from these solutions in large crystals. (Weltzien.)

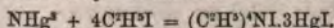
*c. Periodide.* The liquid from which the teriodide has crystallised, yielded, on dilution with water, a heavy, red-brown, oily compound, rich in iodine, and probably consisting of a higher iodide of tetrethylammonium. (Weltzien.)

*Iodomercurates.* *a.*  $C^8H^{20}NI.5HgI^*$ . Obtained by the two following processes: 1. Mercuric iodide boiled with a solution of iodide of tetrethylammonium, is converted into a yellow compound, which melts and collects as a transparent layer at the bottom of the vessel, and, on cooling, solidifies to a brittle mass, having a crystalline fracture. 2. Iodide of tetrethylammonium mixed with a large excess of mercuric chloride forms a whitish crystalline precipitate, which is a mixture of the iodomercurate with a large quantity of the corresponding chlorine-compound:



By boiling with water the latter is removed, while the iodine compound remains. (Hofmann.)

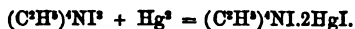
*b.*  $C^8H^{20}NI.3HgI$ . Produced by the action of trimercuramine on iodide of ethyl:



Yellow crystals which dissolve somewhat readily in alcohol, and are not decomposed by water. (R. Müller, Ann. Ch. Pharm. cviii. 6.)

\* Hg = 100.

c.  $C^2H^3NI.2HgI$ . Produced by the action of metallic mercury on teriodide of tetrethylammonium.



The compound dissolves sparingly in water, more easily in hot alcohol, from which it separates on cooling in light yellow, shining, scaly crystals. (H. Risse, Ann. Ch. Pharm., cvii. 224.)

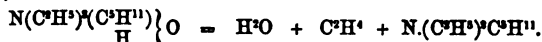
A compound of mercuric iodide with iodide of tetrethylammonium and iodide of mercurotetrethylammonium,



is produced, together with several others, by the action of iodide of ethyl on chloride of dimercurammonium (white precipitate),  $NH^2Hg^2Cl$  (p. 535). It forms yellow crystals, which, after being purified by washing with warm absolute alcohol, resemble mosaic gold, and appear under the microscope as cubes with octahedral and dodecahedral faces. They are decomposed by sunlight, with separation of mercury; melt at  $150^\circ C$ , and decompose at higher temperatures. They are insoluble in water, alcohol, and ether.

Iodide of potassium and iodide of tetrethylammonium dissolve the yellow compound for the most part, with separation of metallic mercury; nitric acid separates mercuric iodide. Its solution in hot hydrochloric acid yields greenish-yellow silky crystals. Chlorine and bromine separate all the iodine after some time, forming crystals with a jetty lustre, resembling naphthalin. When the yellow crystals are heated with recently precipitated oxide of silver, iodide of silver is formed, together with a strongly alkaline liquid, which, after the excess of silver has been removed by sulphuretted hydrogen, contains hydrate of tetrethylammonium. But if the alkaline solution is neutralised with hydrochloric acid, without previous treatment with sulphuretted hydrogen, and evaporated, white crystals are obtained consisting of the compound  $(C^2H^3)^4NCl.HgCl$  (p. 561).

**Triethylamylammonium.**  $C^{11}H^{20}N = N(C^2H^5)^3C^2H^{11}$ . (Hofmann, Chem. Soc. Qu. J. iv. 313.)—The iodide obtained by the action of iodide of amyl on triethylamine forms fine crystals having a fatty lustre, unctuous to the touch, very soluble in water and alcohol, insoluble in ether. The solutions have the bitter taste of quinine. The hydrate,  $N(C^2H^5)^3(C^2H^{11}) \left\{ \begin{smallmatrix} O \\ H \end{smallmatrix} \right\}$ , obtained by heating the iodide with moist oxide of silver, forms an alkaline, very bitter solution, which, when evaporated, yields a non-crystallising syrup. By distillation it is resolved into water, ethylene, and diethylamylamine:



The hydrochlorate forms deliquescent laminae. The chloroplatinate separates from a boiling aqueous solution in splendid orange-yellow needles. The nitrate forms hard needles. The sulphate and oxalate are obtained in gummy masses by evaporation in vacuo.

For bases containing ethyl together with methyl and phenyl, see METHYLAMINES and PHENYLAMINES.

*Ammonium-bases produced by the action of Chloracetic Ether on Triethylamine.*

**Triethyl-oxethylacetylammmonium.**  $C^2H^3O^2N = N \left\{ \begin{smallmatrix} (C^2H^3)^3 \\ C^2H^3(C^2H^3)O^2 \end{smallmatrix} \right\}$ .—When a mixture of triethylamine and chloracetic ether  $[C^2H^3(C^2H^3)ClO^2]$  is heated to  $100^\circ C$ . in a sealed tube, a small quantity of gas burning with a green flame is given off; and chloride of tetrethylammonium is formed, together with the chloride of triethyloxethylacetylammmonium, that is to say, an ammonium in which three at. H are replaced by 3 at. ethyl and the remaining 1 at. H. by a complex molecule containing the elements of chloracetic ether minus the chlorine.

On adding dichloride of platinum to the solution of these chlorides, the chloroplatinate of the complex ammonium-molecule, being slightly soluble, easily separates from the platinum-salt of tetrethylammonium, which is very soluble. Treated with sulphydric acid, it yields the chloride of the complex ammonium, which is very deliquescent. The gold-salt crystallises in needles which melt at  $100^\circ C$ .

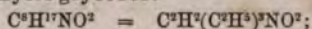
**Triethyl-oxacetylammmonium.**  $C^2H^3O^2N = N \left\{ \begin{smallmatrix} (C^2H^3)^3 \\ C^2H^3O^2 \end{smallmatrix} \right\}$ .—The preceding chloride, treated with oxide of silver, yields chloride of silver and an alcoholic solution that deposits a crystalline substance, which, though perfectly neutral, unites with nitric and hydriodic acids, forming well defined salts. These salts, however, belong to another



series, differing from the preceding by containing an atom of hydrogen in place of ethyl—a difference which is shown by the elimination of alcohol during the reaction. Hence these salts are not *tetrethylic*, like the preceding, but *triethylic*.

The *chloroplatinate*,  $[N.(C^2H^5)^3(C^2H^3O^2)]Cl.PtCl^2$ , forms splendid rhomboïdal prisms. The *chloroaurate* crystallises in needles, moderately soluble in boiling water. The *nitrate* is soluble in alcohol, and is precipitated from the solution by ether in fine needles. The *iodide* forms crystals very soluble in water, and having the composition  $[N.(C^2H^5)^3(C^2H^3O^2)]I.C^2H^5.NO^2$ .

The crystalline substance which remains after the treatment of the tetrethylic chloride (see above) with oxide of silver, is perhaps the monatomic base,  $C^2H^5.NO^2 = N(C^2H^5)^3.(C^2H^3O^2) \left\{ \begin{array}{l} H \\ O \end{array} \right\}$ . It is possible, however, that this compound may split up at the moment of its formation, and that the crystals contain 1 at. water less, having therefore the composition  $C^2H^5.NO^2$ , this being the molecule which enters into the composition of the iodide just mentioned. On this hypothesis, the compound in question would be triethylic glycecol:



it is known, indeed, that glycecol itself has a tendency to form compounds similar in composition to the iodide above mentioned, one of them being represented by the formula  $(C^2H^5.NO^2)Cl.C^2H^5.NO^2$ .

The triethylic compound is not attacked by potash, by boiling nitric acid, or by nitrous acid. When heated, it yields charcoal and a strongly alkaline liquid, which is not triethylamine. (Hofmann, Proc. Roy. Soc. xi. 526; Rép. Chim. pure, 1862, p. 196).

**ETHYLAMMONIUM.** See ETHYLAMINES.

**ETHYLAMYL.** See ETHYL (p. 526).

**ETHYLAMYLCITRIC ACID.**  $C^{12}H^{22}O^7 = \left. \begin{array}{l} C^6H^{10}O^4 \\ C^2H^5 \\ C^2H^3.H \end{array} \right\} O^2$ .—Obtained by saturating a mixture of amylic acid  $[(C^6H^{10}O^4)^m.C^2H^5.H^2.O^2]$  and absolute alcohol with hydrochloric acid gas, then evaporating the alcohol and excess of hydrochloric acid, washing with aqueous carbonate of sodium, dissolving in ether, and decolorising with animal charcoal, as a colourless syrupy liquid, having a very bitter taste and acid reaction. (Breunlin, Ann. Ch. Pharm. xci. 323.)

**ETHYLAMYLIC ETHER.** See AMYL, OXIDE OF (i. 205).

**ETHYL-BASES.** See ETHYLAMINES, ETHYL-ARSINES, ETHYL-PHOSPHINES, &c.

**ETHYL-BENZYLAMINE.** See BENZETHYLAMINE (i. 576).

**ETHYL-BROMANILINE.** See PHENYLAMINE, DERIVATIVES OF.

**ETHYL-BUTYLIC ETHER.** See ETHYL, OXIDE OF (ii. 543).

**ETHYL-CACODYL.** Syn. with ARSENDIETHYL (i. 397).

**ETHYL-CARBAMIC ACID** and **ETHYL-CARBAMIDES.** See CARBAMIC ACID (i. 751), and CARBAMIDE (i. 754).

**ETHYL-CHLORANILINE.** See PHENYLAMINE, DERIVATIVES OF.

**ETHYL-CODEINE** and **ETHYL-CONINE.** See CODEINE (i. 1068), and CONINE (ii. 5).

**ETHYL-CYANAMIDE.** Syn. with CYANETHYLAMIDE (ii. 190).

**ETHYL-CYANANILINE.** See PHENYLAMINE, DERIVATIVES OF.

**ETHYL-DIACETAMIDE.** See ETHYLACETAMIDE (ii. 552).

**ETHYL-DITHIONIC ACID.** Syn. with ethyl-sulphurous acid. (See SULPHUROUS ETHERS.)

**ETHYL-CARBAMIDES**, or *Ethyl-ureas*.—These compounds, derived from carbamide, or urea,  $N^2(CO)^2.H^4$ , by the substitution of ethyl for the whole or part of the hydrogen, have already been partly described under CARBAMIDE (i. 754). The following additional statements have been recently published by Wurtz (Rép. Chim. pure, 1862, 199) and Hofmann (Proc. Roy. Soc. xi. 273; Compt. rend. liv. 252).

*Ethyl-carbamide*.  $N^2(CO)^2.C^2H^5.H^2$ .—Crystallises in oblique rhomboïdal prisms having the obtuse edges truncated. Melts at  $92^\circ C$ . By dry distillation it gives off ammonia and a small quantity of ethylamine, and leaves a residue consisting of a mixture of cyanuric ethers, the chief product being diethylic cyanurate  $C^4[(C^2H^5)^2.H.]N^2O^3$  (p. 293). (Wurtz).

*Diethyl-carbamide*.  $N^2(CO)^2.(C^2H^5)^2.H^2$ .—Colourless, prismatic crystals soluble



in water and alcohol; from the alcoholic solution it separates in silky flexible nondeliquescent needles. Melts at  $109^{\circ}$ — $112.5^{\circ}\text{C}$ . Boils at  $263^{\circ}$  (corrected). When boiled with potash, it gives off ethylamine;  $\text{N}^2(\text{CO})^{\cdot}(\text{C}^2\text{H}^5)^2\text{H}^2 + \text{H}^2\text{O} = \text{CO}^2 + 2(\text{N}.\text{C}^2\text{H}^5.\text{H}^2)$ . It likewise gives off ethylamine when treated with nitrous acid. When chlorine is passed into a solution of diethylcarbamide, a heavy viscid oil is precipitated, partially soluble in water, and having a burning taste and peculiar odour. Nitrate of diethylcarbamide forms rhomboidal prisms, much flattened and extremely deliquescent.

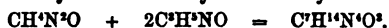
Diethylcarbamide exhibits exactly the same properties, whether prepared by the action of cyanate of ethyl on ethylamine, or of water on cyanate of ethyl. (Wurtz.)

*Triethylcarbamide.*  $\text{C}^3\text{H}^5\text{N}^2\text{O} = \text{N}^2(\text{CO})^{\cdot}(\text{C}^2\text{H}^5)^3\text{H}.$ —Produced by the action of cyanate of ethyl on diethylamine. (Hofmann, Wurtz.)



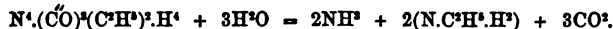
It forms soft crystals, soluble in water, alcohol, and ether, melting at  $63^{\circ}\text{C}$ ., and distilling without decomposition at  $223^{\circ}$  (Hofmann); boils at about  $235^{\circ}$ . (Wurtz.) It does not appear to combine with acids, with chloride of gold, or with chloride of platinum. By the action of alkalis it is resolved into ethylamine, diethylamine, and carbonic anhydride. (Hofmann.)

*Diethyl-tricarbonyl-tetramide* or *-tetramine*.  $\text{C}^2\text{H}^5\text{N}^4\text{O}^2 = \text{N}^4(\text{CO})^2(\text{C}^2\text{H}^5)^2\text{H}^2$ .—This compound, which may be regarded as a carbamide, or urea, of a higher order, is produced by the action of cyanate of ethyl on urea:



It is sparingly soluble in cold water, but dissolves easily in boiling water, and crystallises therefrom in beautiful white scales having a silky lustre. It is easily soluble in alcohol and ether; dissolves also in acids, but not more readily than in water; also in cold potash, and is precipitated unchanged from the solution by acids.

By boiling with potash, however, it is decomposed, yielding ammonia, ethylamine, and carbonic anhydride:



This compound is isomeric with *diethylcyanurate of ammonium*,  $\text{C}^2[(\text{C}^2\text{H}^5)^2\text{NH}^2]\text{N}^2\text{O}^2$ ; but it does not exhibit the characters of an ammonium-salt. (Hofmann.)

The hydrated base produced by the action of cyanuric ether on ethylate of sodium, viz. triethyl-carbonyl-triamine,  $\text{N}^3(\text{CO})^{\cdot}(\text{C}^2\text{H}^5)^3\text{H}^3$  (p. 662), is also related to the ethyl-carbamides.

**ETHYLENE**  $\text{C}^2\text{H}^4$  or  $\text{C}^2\text{H}^2$ . *Olephant gas, Bicarburetted Hydrogen, Heavy Carburetted Hydrogen, Elayl, Ethene, Etherin.*—This compound was discovered in 1795 by four Dutch chemists, Deiman, Paets van Troostwyk, Bondt, and Lauwerenburgh (Crell. Ann. 1795, ii. 195, 310, and 430; Gilb. Ann. ii. 201). It is produced by heating alcohol with strong sulphuric acid or boric anhydride; and by the dry distillation of formates, acetates, butyrates, and many other organic bodies, especially fats, resins, caoutchouc, wood, coal, &c.: it is, therefore, a constituent of coal-gas, being in fact the compound to which that gas chiefly owes its illuminating power. It has also been shown by the experiments of Berthelot (Compt. rend. xliii. 236) that ethylene, as well as other hydrocarbons, may be formed directly from inorganic materials, as when a mixture of disulphide of carbon and sulphuretted or phosphoretted hydrogen is passed over red-hot copper, or more abundantly when a mixture of disulphide of carbon, sulphuretted hydrogen, and carbonic oxide is passed over red-hot iron. A mixture of ethylene with tritylene and marsh-gas is also obtained by the dry distillation of formate of barium; and as formic acid may be produced by the action of carbonic oxide on hydrate of potassium, it follows that the ethylene may be considered, in this case also, as produced from inorganic materials.

*Preparation.*—1. A mixture of 1 vol. strong alcohol and 4 vol. sulphuric acid, is gently heated in a flask or retort, and the evolved gas is passed through two Woulfe's bottles—one containing milk of lime to free it from sulphurous acid, and the other containing strong sulphuric acid to absorb the vapours of ether and alcohol. The mixture soon blackens, and froths considerably towards the end; the frothing may, however, be prevented by adding a sufficient quantity of sand to the mixture to form it into a thick paste. A very good way of conducting the process, given by Mitscherlich (Ann. Ch. Phys. [3] vii. 12), is to boil alcohol of 80 per cent. in a flask, and pass the vapour into a boiling mixture of 10 pts. strong sulphuric acid and 3 pts. water (boiling point  $160$ — $165^{\circ}\text{C}$ ). In this case, the mixture does not blacken, and the gas obtained is free from sulphurous acid; but it requires to be purified from ether and

alcohol vapour as before. The action consists ultimately in a dehydration of the alcohol;  $C^2H^4O - H^2O = C^2H^4$ ; but it is probable that ethylsulphuric acid is first formed, and yields ethylene by its subsequent decomposition,  $C^2H^4.H.SO^4 = C^2H^4 + H^2SO^4$ .

2. Absolute alcohol is mixed with four times its weight of fused boric anhydride, and the mixture gently heated in a retort. A large quantity of ethylene gas is then evolved, which may be rendered pure by mere washing with water. The residue in the retort serves for a fresh operation. The only inconvenience of this method is, that the delivery-tubes are apt to become stopped up by solid boric anhydride mechanically carried over: hence it is necessary to use very wide tubes. (Ebelmen, Ann. Ch. Phys. [3] xvi. 136.)

*Properties.*—Ethylene is a colourless gas, having a faint ethereal odour; if quite free from ether-vapour, it would probably be destitute of odour; it is irrespirable. Its specific gravity is 0.9784 (Saussure), answering to a condensation to 2 vol. (by calculation,  $\frac{2.12 + 4.1}{2} \times 0.0693 = 0.9702$ ). When exposed to strong pressure, at a

temperature of  $-110^\circ C$ , it condenses to a limpid liquid, which does not solidify.

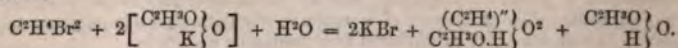
Ethylene gas is nearly insoluble in water, and dissolves but sparingly in alcohol (see GASES, ABSORPTION OF); ether dissolves it more freely. It is likewise absorbed by cuprous chloride.

*Decompositions.*—Ethylene passed through a red-hot tube is resolved into marsh-gas and free carbon,  $C^2H^4 = CH^4 + C$ . It is very inflammable, and burns in the air with a bright white flame; probably undergoing in the flame the same decomposition as when passed through a red-hot tube, so that the marsh-gas burns, and the separated particles of carbon, being rendered incandescent by the high temperature thus produced, give to the flame its peculiar brightness. Mixed with a quantity of oxygen just sufficient for complete combustion, it explodes violently when brought in contact with flame, or when an electric spark is passed through the mixture. 2 vols. ethylene, containing 2 at. C and 4 at. H, consume 6 at. or 6 vol. O, and produce 4 vol.  $CO^2$  besides water. In chlorine gas, ethylene burns with a very smoky flame,  $C^2H^4 + Cl^4 = 4HCl + C^2$ . A mixture of 1 vol. ethylene and 2 vol. chlorine burns slowly when set on fire, depositing a very large quantity of charcoal.

*Combinations.*—Ethylene is a diatomic radicle, uniting with 2 at. chlorine, bromine, cyanogen, and other monatomic radicles, and with 1 at. oxygen, sulphur, and other diatomic radicles. With the elements of 2 at. peroxide of hydrogen, it forms hydrate of ethylene, ethylenic alcohol, or glycol, and with the peroxides of various acid radicles it forms ethers, which are acid, neutral, or basic, according to the proportions of the combination. With chlorine, bromine, iodine, pernitric oxide, and the chlorides of sulphur, it unites directly. It is quickly absorbed by sulphuric anhydride, and by Nordhausen sulphuric acid, forming ethionic anhydride (p. 524) and isethionic acid. When briskly and continuously agitated with ordinary strong sulphuric acid,  $H^2SO^4$ , it unites therewith, forming ethylsulphuric acid,  $C^2H^4.SO^4$  (Berthelot, Ann. Ch. Pharm. xciv. 78). When it is heated for some time to  $100^\circ C$ . with hydriodic acid, the two combine, forming iodide of ethyl,  $(C^2H^4 + HI = C^2H^5I)$ . A similar action takes place with hydrobromic acid, but less readily; and with hydrochloric acid it is very slow indeed. (Berthelot, Ann. Ch. Pharm. civ. 184; cxv. 114.)

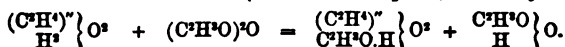
**ETHYLENE, ACETATES OF.** (Wurtz, Compt. rend. xliii. 199; Ann. Ch. Pharm. c. 110; Ann. Ch. Phys. [3] lv. 400. Atkinson, Phil. Mag. [4] xvi. 433; Ann. Ch. Pharm. cix. 232.

*Monoacetate.*  $C^2H^4O^3 = \frac{(C^2H^4)^n}{C^2H^4O.H} O^2 = (C^2H^4)^n.C^2H^4O^2.HO$ . *Monoacetic glycol, Glycolic monoacetin.*—Obtained: 1. By the action of bromide of ethylene on acetate of potassium:



1 pt. of pure bromide of ethylene and 1 pt. of acetate of potassium, together with 2 pts. of 85 per cent. alcohol, are heated for two days to  $100^\circ C$ . in a strong flask (a soda-water bottle answers very well) securely corked. Bromide of potassium is then formed, together with a colourless liquid containing monoacetate of ethylene, acetic acid, and acetic ether (formed by the action of the acetic acid on the alcohol), besides alcohol and water. On distilling it, monoacetate of ethylene mixed with acetic acid passes over between  $130^\circ$  and  $180^\circ C$ , and nearly pure monoacetate from  $180^\circ$  to  $185^\circ$ . By repeated rectification of these liquids, the pure monoacetate is obtained, boiling at  $182^\circ$ . In the first distillation, the liquid often jumps violently, in consequence of the separation of a little bromide of potassium; in this case an equal volume of ether must be added to precipitate the bromide of potassium, and the liquid filtered

(Atkinson). Maxwell Simpson recommends, especially for the preparation of large quantities of the monoacetate, to heat the materials, not in a closed vessel, but in a large flask connected with a Liebig's condenser, in such a manner as to cause the condensed vapour to flow back into the vessel. A considerable quantity of diacetate of ethylene is formed at the same time as the monoacetate in this reaction (Lourengo).—2. By the action of acetate of potassium on *chloride of ethylene*. The decomposition does not take place so readily as with the bromide, and requires the mixture to be heated for three or four days (Atkinson).—3. By heating a mixture of 1 at. glycol and 1 at. acetic anhydride in a sealed tube for several hours at a temperature not exceeding 170° C., and collecting apart the liquid which, in the subsequent distillation, passes over between 180° and 186° C. (Maxwell Simpson, Proc. Roy. Soc. ix. 726.)

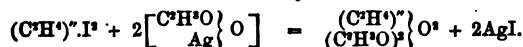


4. By heating 1 at. ethylenic alcohol (glycol) with 1 at. acetic acid to 200° C. in a sealed tube. (Lourengo.)

Monoacetate of ethylene is a colourless, oily liquid, boiling at 182° C. It is heavier than water, and miscible with water and with alcohol. The aqueous solution is neutral. It is easily decomposed by potash or baryta, yielding hydrate of ethylene, and an acetate of the base.

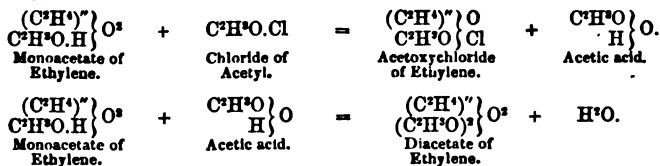
*Monethylenic Diacetate.*  $\text{C}^{\text{H}}\text{H}^{\text{O}}\text{O}^{\text{H}} = \left\{ \begin{smallmatrix} \text{C}^{\text{H}}\text{H}^{\text{H}} \\ \text{C}^{\text{H}}\text{H}^{\text{O}}\text{O} \end{smallmatrix} \right\} \text{O}^{\text{H}} = (\text{C}^{\text{H}}\text{H}^{\text{H}})^{\text{H}}.(\text{C}^{\text{H}}\text{H}^{\text{O}}\text{O})^{\text{H}}$ .—Produced:

1. By the action of iodide or bromide of ethylene on acetate of silver:



Iodide of ethylene is mixed by small portions with well-dried acetate of silver, and the mixture is introduced into a flask. A brisk action soon begins, and the mass assumes a yellow colour, from formation of iodide of silver, and gives off a considerable quantity of gas, principally carbonic anhydride and ethylene (arising from secondary actions). As soon as the mixture is sufficiently cooled, a fresh portion is introduced, and the process continued till between 100 and 150 grammes of iodide of ethylene have been used. At the end of the reaction, there is found in the flask a yellow mass of iodide of silver saturated with a liquid; and on distilling this mixture, which requires a somewhat high temperature, an acid liquid passes over, coloured brown by iodine, and containing acetic acid besides neutral products. When subjected to fractional distillation, it begins to boil at 120° C., but the temperature soon rises, and the portion which distils over between 160° and 200° must be collected apart. The distillate, which is still acid, is redistilled over oxide of lead, and again subjected to fractional distillation, till it passes over almost entirely between 180° and 190°. If it still contains a trace of iodide, it must be rectified over oxide of silver (Wurtz). Bromide of ethylene is, however, to be preferred to the iodide for this preparation, because it is more easily obtained and has a lower atomic weight. (Wurtz.)

2. By heating monoacetate of ethylene with chloride of acetyl in a sealed tube to 100° C. for a day, the action taking place in two stages, as shown by the following equations:—



Two layers of liquid are thus formed, the lower consisting of water, the upper of diacetate and acetoxychloride of ethylene. (Lourengo, Ann. Ch. Pharm. cxiv. 126.)

It is a colourless neutral liquid, nearly inodorous at common temperatures, but smelling slightly of acetic acid when heated. Specific gravity = 1.128 at 0° C. Boiling point 186°—187° C. Vapour-density = 4.744.

When poured into a small quantity of water, it sinks to the bottom in the form of an oil. It dissolves in 7 pts. of water at 22°, and is separated from the solution by chloride of calcium. Alcohol and ether dissolve it in all proportions (Wurtz). By bases, in presence of water, it is resolved into acetic acid and hydrate of ethylene. (Wurtz.)

*Polyethylenic Diacetates.*—These ethers, which may be regarded as compounds of acetic anhydride,  $\text{C}^{\text{H}}\text{H}^{\text{O}}\text{O}^{\text{H}}$ , with 2, 3, 4, &c., molecules of oxide of ethylene, are pro-



duced, together with monethylenic diacetate, by heating oxide of ethylene with glacial acetic acid or acetic anhydride, and may be separated by fractional distillation. The first portion of the distillate consists of monethylenic diacetate, after which there pass over successively:

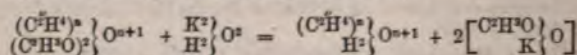
*Diethylenic diacetate*,  $\left\{ \begin{smallmatrix} \text{C}^2\text{H}^4\text{O}^2 \\ \text{C}^2\text{H}^4\text{O}^2 \end{smallmatrix} \right\} \text{O}^2 = (\text{C}^2\text{H}^4\text{O})^2 \cdot \text{C}^2\text{H}^4\text{O}^2$ , boiling at about  $250^\circ \text{C}$ .

*Triethylenic diacetate*,  $\left\{ \begin{smallmatrix} \text{C}^2\text{H}^4\text{O}^2 \\ \text{C}^2\text{H}^4\text{O}^2 \end{smallmatrix} \right\} \text{O}^4 = (\text{C}^2\text{H}^4\text{O})^3 \cdot \text{C}^2\text{H}^4\text{O}^2$ , boiling at about  $290^\circ \text{C}$ .

*Tetreethylenic diacetate*,  $\left\{ \begin{smallmatrix} \text{C}^2\text{H}^4\text{O}^2 \\ \text{C}^2\text{H}^4\text{O}^2 \end{smallmatrix} \right\} \text{O}^6 = (\text{C}^2\text{H}^4\text{O})^4 \cdot \text{C}^2\text{H}^4\text{O}^2$ , a viscid liquid which boils above  $300^\circ \text{C}$ . under the ordinary atmospheric pressure, and requires to be distilled in a rarefied atmosphere.

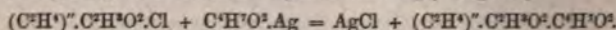
The same compounds may be produced by the combination of neutral diethylenic acetate with 1, 2, 3, &c., molecules of oxide of ethylene.

Each of them, when distilled with potash, yields the corresponding polyethylenic alcohol, the general equation of the decomposition being:



**ETHYLENE, ACETOBUTYRATE OF.**  $\text{C}^2\text{H}^4\text{O}^4 = \left\{ \begin{smallmatrix} \text{C}^2\text{H}^4\text{O}^2 \\ \text{C}^2\text{H}^4\text{O} \end{smallmatrix} \right\} \text{O}^2 =$

$(\text{C}^2\text{H}^4\text{O})^2 \cdot \text{C}^2\text{H}^4\text{O}^2 \cdot \text{C}^2\text{H}^4\text{O}^2$ . (Maxwell Simpson, Proc. Roy. Soc. x. 115.)—Obtained: 1. By heating equivalent quantities of butyrate of silver and acetoxychloride of ethylene to  $100^\circ$ — $120^\circ \text{C}$ ., or of acetate of silver and butyroxylchloride of ethylene to  $150^\circ$ , then digesting with ether, filtering, and distilling (Simpson):



2. By heating monoacetate of ethylene with butyric acid or chloride of butyryl, or monobutyrate of ethylene with acetic acid or chloride of acetyl (Lourenço). It is a colourless liquid, having a bitter, pungent taste, heavier than water, insoluble in water, soluble in alcohol. It is very stable, being but slowly decomposed by aqueous potash, even at the boiling heat. (Simpson.)

**ETHYLENE, ACETOVALERATE OF.**  $\text{C}^2\text{H}^4\text{O}^4 = (\text{C}^2\text{H}^4\text{O})^2 \cdot \text{C}^2\text{H}^4\text{O}^2 \cdot \text{C}^2\text{H}^4\text{O}^2$ . (Lourenço, Ann. Ch. Pharm. cxiv. 122.)—Obtained by heating monoacetate of ethylene with valeric acid, or *vice versa*. Colourless, oily, neutral liquid, boiling at about  $230^\circ \text{C}$ ., insoluble in water, soluble in alcohol and ether.

**ETHYLENE, ACETOXYCHLORIDE OF.**  $\text{C}^2\text{H}^4\text{ClO}^2 = (\text{C}^2\text{H}^4\text{O})^2 \cdot \text{C}^2\text{H}^4\text{O}^2 \cdot \text{Cl}$ . *Glycol chloracetique, Glycolic Chloracetin*. (Maxwell Simpson, x. 114.)—Obtained by passing dry hydrochloric acid gas into monoacetate of ethylene at  $100^\circ \text{C}$ ., precipitating with water, washing, drying, and rectifying. It is a colourless liquid, having a specific gravity of 1.1783 at  $0^\circ \text{C}$ . Boils at  $145^\circ$  without decomposition. Vapour-density by observation = 4.369; by calculation (2 vol.) = 4.244.

**ETHYLENE, ACETOXYIODIDE OF.**  $\text{C}^2\text{H}^4\text{IO}^2 = (\text{C}^2\text{H}^4\text{O})^2 \cdot \text{C}^2\text{H}^4\text{O}^2 \cdot \text{I}$ . *Glycol iodacetique, Glycolic Iodacetin*.—Obtained by passing hydriodic acid gas into monoacetate of ethylene, or a mixture of equivalent quantities of glacial acetic acid and glycol, externally cooled, till a portion of the liquid gives a considerable oily precipitate on the addition of water; if the passage of the gas be further continued, iodide of ethylene is likely to be formed. The product is well washed with very dilute potash and dried in vacuo.

Glycolic iodacetin is, at ordinary temperatures, an oily liquid, having a sweetish pungent taste; at low temperatures it crystallises in tables. It sinks in water, and is insoluble in that liquid, but dissolves in alcohol and ether. Heated with potash, it yields iodide of potassium, acetate of potassium, and oxide of ethylene. (Simpson.)

**ETHYLENE, BENZOATE OF.**  $\text{C}^2\text{H}^4\text{O}^4 = \left\{ \begin{smallmatrix} \text{C}^2\text{H}^4\text{O}^2 \\ \text{C}^2\text{H}^4\text{O} \end{smallmatrix} \right\} \text{O}^2$ . *Glycolic Dibenzoate*.—68 grms. of benzoate of silver (rather more than 2 at.) and 29 grms. bromide of ethylene are heated for several days to  $100^\circ \text{C}$ . in a long-necked flask; the product is taken up with ether, and the solution treated with a small quantity of slaked lime, then filtered and distilled in the water-bath. The residue on cooling becomes filled with crystals, which are to be separated from the mother-liquor, pressed between paper, and purified by several recrystallisations from ether.

By spontaneous evaporation of the ethereal solution, the compound is deposited in

shining, colourless, right rhomboidal prisms, which melt at  $67^{\circ}\text{C}$ ., forming a liquid which boils at a temperature above the boiling point of mercury, and distils without alteration. It is easily decomposed by heating with potash, yielding hydrate of ethylene and benzoate of potassium. (Wurtz, Ann. Ch. Phys. [3] lv. 437.)

**ETHYLENE, BROMIDE OF.**  $\text{C}^2\text{H}^2\text{Br}^2$ .—This compound was discovered by Balard in 1826 (Ann. Ch. Phys. [2] xxxii. 375); further examined by Löwig (*Das Brom und sein chemisches Verhalten*, Heid. 1829, p. 47), Serullas (Ann. Ch. Phys. [2] xxxix. 228), D'Arcet (L'Institut, 1836, No. 106; J. pr. Chem. v 28), and Regnault (Ann. Ch. Phys. [2] lix. 358). It is produced by the direct combination of bromine with ethylene. Bromine gradually dropped into ethylene-gas quickly loses its colour, absorbs the gas, and is converted into bromide of ethylene, which may be purified by washing it with alkaline water, and then distilling over sulphuric acid and caustic baryta alternately (Balard). As the combination is attended with great evolution of heat, which may occasion loss of bromine, it is usually recommended to pass a stream of ethylene-gas through bromine covered with a layer of water; unless, however, the current of gas is very slow, there is great risk of both ethylene and bromine being carried off uncombined. The following is a good method of preparation:—A strong glass bottle of 2 or 3 litres capacity is provided with a perforated cork, through which is fitted a glass tube open at both ends, and reaching nearly to the bottom of the bottle, while the upper end, slightly projecting over the cork, communicates by means of a flexible caoutchouc-tube, with a gas-holder containing ethylene. To start the operation, the bottle is detached and filled over water with ethylene-gas, into which are then poured from 100 to 130 grms. of commercial bromine and about half that quantity of water, the cork with the glass tube being immediately replaced. On gently agitating the bottle, the ethylene is rapidly absorbed, and on turning the stop-cock of the gas-holder, the gas rushes into the bottle as into a vacuum. If the agitation be continued, a very large volume of ethylene may be thus united with the bromine in a very short time, without the loss of a particle of the constituents or of the compound. (Hofmann, Chem. Soc. Qu. J. xiii. 67.)

Bromide of ethylene is a colourless, fragrant liquid, which solidifies to a crystalline mass at about  $0^{\circ}\text{C}$ ., melts at  $9^{\circ}$ , and boils at  $129^{\circ}$ . Specific gravity = 2.16. Vapour-density = 6.485 (Regnault); by calculation (2 vol.) = 6.564. It is insoluble in water, but soluble in alcohol and in ether.

Bromide of ethylene is decomposed by *alcoholic potash*, which abstracts the elements of a molecule of hydrobromic acid, leaving bromethylene or bromide of vinyl,  $\text{C}^2\text{H}^2\text{Br}$ . With *sulphhydrate of potassium* it yields sulphhydrate of ethylene,  $\text{C}^2\text{H}^2.\text{H}^2.\text{S}^2$ ; with *monosulphide and disulphide of potassium*, it yields mono- and disulphide of ethylene. With *acetate of silver* it yields diacetate of ethylene (p. 567), and acts in like manner on other silver-salts. With *acetate of potassium*, dissolved in aqueous alcohol, it forms monoacetate of ethylene (p. 567). According to Lourenço, the first product of the action is diacetate of ethylene, which is then resolved by the water present into monoacetate of ethylene and acetic acid (or by the alcohol into monoacetate of ethylene and acetic ether). Heated with *cyanide of potassium*, it yields cyanide of ethylene,  $\text{C}^2\text{H}^2\text{Cy}^2$  (Simpson, i. 314). With *ammonia* it forms ethylene-diamine, diethylene-diamine, and triethylene-diamine. For the reactions with *ethylamine*, *phenylamine*, *triethylphosphine*, and other organic bases, see AMMONIUM-BASES (i. 196); also ETHYLENE-BASES and PHOSPHORUS-BASES.

#### Brominated Derivatives of Bromide of Ethylene.

Bromide of ethylene is decomposed by alcoholic potash, which abstracts the elements of one molecule of hydrobromic acid, leaving monobromethylene,  $\text{C}^2\text{H}^2\text{Br}$ . This compound, like ethylene itself, unites with 2 at. bromine, forming  $\text{C}^2\text{H}^2\text{Br}^2$ , which is in like manner attacked by alcoholic potash, yielding dibromethylene; and by continuing this alternate treatment with alcoholic potash and bromine, the two following series of compounds are obtained:

Bromethylene . . .	$\text{C}^2\text{H}^2\text{Br}$	Dibromide of Bromethylene . . .	$\text{C}^2\text{H}^2\text{Br}.\text{Br}^2$
Dibromethylene . . .	$\text{C}^2\text{H}^2\text{Br}^2$	Dibromide of Dibromethylene . . .	$\text{C}^2\text{H}^2\text{Br}^2.\text{Br}^2$
Tribromethylene . . .	$\text{C}^2\text{HBr}^3$	Dibromide of Tribromethylene . . .	$\text{C}^2\text{HBr}^3.\text{Br}^2$
Tetrabromethylene or Dibromide of Carbon }	$\text{C}^2\text{Br}^4$	Dibromide of Tetrabromethylene, or Tribromide of Carbon }	$\text{C}^2\text{Br}^4.\text{Br}^2$

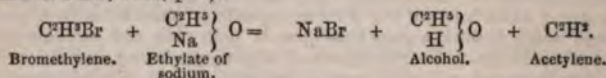
Bromethylene was discovered by Regnault (Ann. Ch. Phys. [2] lix. 358); the rest, with the exception of  $\text{C}^2\text{Br}^4$  and  $\text{C}^2\text{Br}^3$ , were first obtained by Cahours (Compt. rend. xxxi. 293), who did not particularly describe them; he observed, however, that the bromides of the bromethylenes are more easily attacked by alcoholic potash, in



proportion as they contain more bromine, the reaction yielding, in addition to bromide of potassium and a brominated ethylene, potassium-salts of peculiar brominated acids which have not been examined.

**Bromethylene or Bromide of Vinyl.**  $C^2H^3Br$ .—A mixture of bromide of ethylene and alcoholic potash heated to  $30^\circ$  or  $40^\circ$  C. gives off a gas which, when purified by passing through water, then over chloride of calcium, and condensed in a receiver surrounded with ice and salt, yields bromethylene as a colourless, very mobile liquid, having an alliaceous, ethereal odour. Specific gravity about 1.52. Boils at ordinary temperatures. Vapour-density = 3.691 (Regnault). When kept in a sealed tube it sometimes solidifies to a white amorphous mass of the same composition, having the appearance of porcelain, insoluble in water, alcohol, and ether; this solid modification when heated becomes carbonised, with violent evolution of hydrobromic acid. (Hofmann, Chem. Soc. Qu. J. xiii. 68.)

Potassium heated with bromethylene decomposes it, with ignition. Chlorine attacks it, forming an oily substance (Regnault). With *ethylate* or *amylate* of sodium, it yields bromide of sodium, ethylic or amylic alcohol, and acetylene (Sawitsch, Bull. Soc. Chim. de Paris, 1861, p. 7):



A similar transformation takes place when bromethylene is passed into an ammoniacal solution of nitrate of silver, the silver-compound of acetylene being then produced. (Miasnikoff, *ibid.* p. 12.)

**Bromide of Bromethylene.**  $C^2H^3Br^2 = C^2H^4Br.Br^2$ .—Obtained by adding bromine by small portions to bromethylene contained in a long-necked flask surrounded by a freezing mixture; purified by washing with alkaline, and with pure water, drying with chloride of calcium, and rectification. It is a colourless liquid, having an odour somewhat like that of chloroform. Specific gravity = 2.620 at  $23^\circ$  C. Boils at  $186.5^\circ$  C. (Wurtz, Ann. Ch. Phys [3] li. 84.)

Alcoholic potash converts it, partly into dibromethylene, partly into monobromethylene, and the latter, by the further action of the alcoholic potash, is decomposed in the manner above mentioned, yielding among other products acetylene (Sawitsch), and bromacetylene (Reboul). If the bromide of bromethylene is added by drops to a boiling solution of alcoholic potash contained in a flask from which the air has been expelled by boiling the liquid for a short time, and the evolved vapours are freed from admixed alcohol and dibromethylene by passing them through two or three wash-bottles containing water, and in which the air has been replaced by carbonic anhydride, a considerable quantity of gas is obtained, which, when freed from carbonic anhydride by potash, is spontaneously inflammable, and is found to consist of a mixture of acetylene,  $C^2H^2$ , and bromacetylene,  $C^2HBr$ . (Reboul, Ann. Ch. Pharm. cxxiv. 267.)

**Dibromethylene.**  $C^2H^2Br^2$ .—Produced from the preceding compound,  $C^2H^3Br^2$ , by the action of sodium, of solid hydrate of potassium, or of alcoholic potash. When solid potash is used, the action is so violent that the dibromethylene distils over almost instantly. With alcoholic potash the action is more moderate; and by dropping the bromide of bromethylene into boiling alcoholic potash, separating the resulting products as above described, and rectifying the liquid collected in the first wash-bottle, the dibromethylene is obtained pure.

Dibromethylene is a colourless, limpid liquid, which, in contact with the air, becomes turbid and deposits a white substance of isomeric composition; having a specific gravity of  $3.053$  at  $14.5^\circ$  C.; insoluble in water, alcohol, and ether, nearly insoluble in disulphide of carbon; not attacked by mineral acids at mean temperature; decomposed by aqueous ammonia, slowly in the cold, more quickly and completely at  $100^\circ$  C., with formation of bromide of ammonium and separation of a carbonaceous substance. Aqueous potash acts in like manner but more slowly. (Sawitsch, Jahresber. d. Chem. 1860, p. 430.)

**Dibromide of Dibromethylene.**  $C^2H^2Br^4 = C^2H^4Br^2.Br^2$ . (Lennox, Chem. Soc. Qu. J. xiii. 206.—Reboul, *loc. cit.*).—Produced: 1. By the direct combination of bromine with dibromethylene, which takes place with great energy (Lennox).—2. By passing acetylene gas into bromine, the compound  $C^2H^2$  then taking up 4 at. Br. (Reboul). When purified by washing and rectification, it boils at about  $200^\circ$  C., but with partial decomposition, giving off vapours which powerfully attack the eyes. When exposed to a freezing mixture, it solidifies to a white crystalline mass. It is insoluble in water, but easily soluble in alcohol and ether (Lennox). Specific gravity 2.88 at  $22^\circ$  C. (Reboul.)

**Tribromethylene.**  $C^2HBr^3$ .—Obtained by treating the last compound with alcoholic potash, and precipitating with water. It is an oily liquid boiling at  $130^\circ$  C.,



and apt to change spontaneously into an isomeric solid, easily soluble in alcohol and in ether, from which it crystallises in colourless plates. An alcoholic or ethereal solution of the oily modification likewise yields the crystalline solid by slow evaporation. (Lennox, *loc. cit.*)

**Dibromide of Tribromethylene.**  $C^3HBr^3 = C^3HBr^2.Br^2$ .—Obtained: 1. By cautiously distilling tribromethylene into a receiver containing bromine. Combination takes place with considerable energy, and the product, after washing with weak potash and with water, is a yellowish-red oil, soluble in alcohol and ether, and solidifying when exposed to a frigorific mixture. (Lennox, *loc. cit.*)

2. By the action of bromine on bromacetylene,  $C^2HBr$ . When the gaseous mixture of this compound and acetylene (p. 570) is passed into bromine covered with a layer of water (to moderate the action, which is otherwise so violent as to set the gas on fire), each of these bodies takes up 4 at. bromine, forming the compounds  $C^2H^2Br^4.Br^2$ , and  $C^2HBr^3.Br^2$ , and a liquid is obtained, which, when freed from excess of bromine by aqueous potash, and sufficiently cooled, deposits the latter compound in crystals, while the former remains liquid. (Reboul.)

Dibromide of tribromethylene is insoluble in water, but soluble in alcohol and ether (Lennox, Reboul), especially at the boiling heats of these liquids, and crystallises from its alcoholic solution in beautiful prisms. It smells like camphor, melts at  $48^\circ$ – $50^\circ$  C., and is decomposed by distillation. (Reboul.)

**Tetrabromethylene or Dibromide of Carbon.**  $C^2Br^4$ .—Produced by the action of alcoholic potash on the compound,  $C^2HBr^3$  (Lennox), also by that of bromine on alcohol or ether (Löwig). It is a white crystalline solid. For its properties and reactions see vol. i. page 764.

**Dibromide of Tetrabromethylene or Tribromide of Carbon.**  $C^2Br^4 = C^2Br^3.Br^2$ .—Obtained: 1. By heating bromine in a sealed tube with dibromide of carbon.—2. By heating either of the compounds,  $C^2H^2Br^4$  or  $C^2HBr^3.Br^2$ , with bromine and water in sealed tubes to  $100^\circ$  C. for 15 to 20 hours, or better to  $180^\circ$  for a few hours. Hydrobromic acid is then formed, and as the tube cools, the compound  $C^2Br^4$  is deposited in crystals; the remaining liquid, which still smells of bromine, deposits, when left to evaporate, a mixture of tribromide of carbon and dibromide of tribromethylene, which may be separated by alcohol. The formation of tribromide of carbon is represented by the equations:



and



Tribromide of carbon is but very slightly soluble in alcohol and ether, even at the boiling heats of these liquids, but dissolves easily in sulphide of carbon, and separates from the solution by spontaneous evaporation in hard, rather thick, transparent crystals, having the form of right rectangular prisms, with truncation of the lateral and two of the basal edges. When heated, it decomposes, before melting, at  $200^\circ$ – $210^\circ$  C. into bromine and dibromide of carbon. (Reboul, *Ann. Ch. Pharm.* cxxiv. 271.)

**ETHYLENE, BUTYRATE OF.**  $C^2H^2O^2 = \frac{(C^2H^2)^2}{(C^2H^2O^2)^2} O^2 = (C^2H^2)^2$ .  
( $C^2H^2O^2$ ) $^2$ .—Obtained by heating for several hours, in the water-bath, a paste composed of 90 grms. (2 at.) butyrate of silver, 48 grms. (1 at.) of bromide of ethylene, and a sufficient quantity of butyric acid, exhausting the product with ether, and distilling. After the ether has passed over, the greater part of the remaining liquid distils between  $230^\circ$  and  $240^\circ$  C., and by fractional distillation butyrate of ethylene is obtained, boiling between  $239^\circ$  and  $241^\circ$ .

Colourless liquid, having a strong butyric odour, which is rather persistent when the liquid is rubbed on the skin. Specific gravity 1.024 at  $0^\circ$  C. Boils at about  $240^\circ$ , and distils without alteration. Perfectly insoluble in water, but dissolves in all proportions in alcohol or ether. (Wurtz.)

**ETHYLENE, BUTYROXYCHLORIDE OF.**  $C^2H^2ClO^2 = (C^2H^2)^2.C^2H^2O^2.Cl$ .  
*Glycolic Chlorobutyrim, Glycol Chlorobutyrique.* (Simpson, *loc. cit.*)—Prepared like the acetoxychloride (p. 568). Colourless liquid, having a pungent, somewhat bitter taste; insoluble in water, freely soluble in alcohol. Specific gravity 1.0854 at  $0^\circ$  C. Boiling point about  $190^\circ$ .

**ETHYLENE, CHLORIDE OF.**  $C^2H^2Cl^2$ . *Dutch liquid.*—This compound was discovered in 1795 by the Dutch chemists, Deiman, Paets van Troostwyk, Bondt, and Lauwerenburgh (*Crell. Ann.* ii. 200), and has been further examined by Liebig (*Ann. Ch. Pharm.* i. 213; ix. 20), Dumas (*Ann. Ch. Phys.* [2] xlviii. 186), Laurent (*ibid.* lxiii. 377), Regnault (*ibid.* lviii. 301; lxi. 261; lxxi. 371), Mala-

guti (Ann. Ch. Phys. [3] xvi. 6 and 14), and Pierre (Compt. rend. xxv. 130).—See also Gm. (viii. 162). It is easily produced by bringing ethylene gas in contact with moist chlorine (the gases scarcely act upon each other when dry), or with a metallic perchloride, which easily gives up part of its chlorine, or by the action of pentachloride of phosphorus on hydrate of ethylene.

*Preparation.*—Ethylene gas, produced by heating a mixture of alcohol and sulphuric

Fig. 470.



acid (p. 565), is passed through a wash-bottle containing potash to free it from sulphurous acid; through a second containing alcohol, which removes vapour of ether; and sometimes through a third containing water to free it from alcohol-vapour. It then passes into a large glass globe (fig. 470), having a long neck, which descends into a bottle closed with a cork, and after the stream of gas has been continued long enough to expel the air, moist chlorine from another flask is also admitted into the globe. The two gases then unite, forming an oily liquid, which runs down into the receiver.

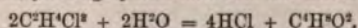
2. Ethylene gas is passed through the tubulus of a retort containing a slightly heated mixture for the evolution of chlorine (2 pts. black oxide of manganese, 3 pts. common salt, 4 pts. water, and 5 pts. sulphuric acid), and the chloride of ethylene thus formed is distilled off. This process may be employed for the preparation of chloride of ethylene by means of coal-gas instead of pure ethylene. (Limpricht.)

3. Ethylene gas is passed into pentachloride of antimony (produced by saturating ordinary butter of antimony with chlorine, i. 318), and the product is distilled, till the distillate no longer yields any oil on addition of water. The oily chloride of ethylene is then decanted, shaken up with oil of vitriol till it no longer blackens, then distilled over a water-bath.

The product obtained by either of these methods is purified by washing, first with alkaline, then with pure water, dried by contact with chloride of calcium, and rectified.

*Properties.*—Dichloride of ethylene is a colourless, neutral, oily liquid, having a fragrant ethereal odour, and a sweetish aromatic taste. Specific gravity = 1.247 at 18° C. (Liebig); 1.256 at 12° (Regnault). It boils at 82.5 under a pressure of 765 mm. (Regnault), at 85° under a pressure of 770 mm. (Dumas). Vapour-density = 3.4434 (Gay-Lussac), by calculation (2 vol.) = 3.4303. It is nearly insoluble in water, to which, however, it imparts its odour, but soluble in alcohol and ether. It dissolves a considerable quantity of phosphorus when heated therewith. It may be mixed, and even distilled, with strong sulphuric acid, without alteration.

*Decompositions.*—1. Dichloride of ethylene is inflammable, and burns with a green, very smoky flame, giving off vapours of hydrochloric acid.—2. When passed in the liquid state through a red-hot tube, it deposits carbon, and yields a mixture of hydrochloric acid gas and a hydrocarbon which burns with a bluish flame.—3. Passed in the state of vapour through a red-hot tube, it yields chloride of carbon, free carbon, and crystals of naphthalin.—4. When covered with water and exposed to sunshine, it is gradually decomposed, yielding hydrochloric acid and acetate of ethyl:



5. Chlorine, especially under the influence of heat or light, transforms it into mono-, di-, tri-, and per-chlorethylene.—6. Ammonia gas does not act upon liquid dichloride of ethylene, but when mixed with the vapour, it forms sal-ammoniac and unflammable gas (Robiquet and Colin, Ann. Ch. Phys. [2] i. 213, ii. 206).—7. The dichloride,

heated in sealed tubes with *alcoholic ammonia*, yields the bases  $C^2H^4.H^1.N^2$ ,  $(C^2H^4).H^2.N^2$ , and  $(C^2H^4).N^2$  (see ETHYLENE-BASES).—8. *Potassium* attacks it violently, forming a porous mass, and eliminating a mixture of hydrogen and chlor-ethylene:



9. It is scarcely attacked by aqueous potash, but by *alcoholic potash*, or *ethylate of potassium* (or sodium), it is resolved into hydrochloric acid and chloroethylene,  $C^2H^4.Cl$ .—10. With *sulphydrate*, *monosulphide*, *disulphide*, and *sulphocyanate of potassium*, it yields the corresponding salts or ethers of ethylene.

#### Chlorinated Derivatives of Chloride of Ethylene.

Dichloride of ethylene subjected to the continued action of chlorine yields the several chlorinated dichlorides contained in the left-hand column of the following table, and each term of this series (beginning with  $C^2H^4.Cl^2$ ), when treated with alcoholic potash, gives up 1 at. HCl, and yields the compound standing opposite to it in the right-hand column.

Dichloride of Ethylene	$C^2H^4.Cl^2$	Chlorethylene	$C^2H^4.Cl$
Monochlorinated	$C^2H^4.Cl.Cl^2$	Dichlorethylene	$C^2H^4.Cl^2$
Dichlorinated	$C^2H^4.Cl^2.Cl^2$	Trichlorethylene	$C^2H^4.Cl^3$
Trichlorinated	$C^2H^4.Cl^3.Cl^2$	Perchlorethylene	$C^2Cl^4$
Perchlorinated	$C^2Cl^4.Cl^2$		

These compounds are precisely analogous to the brominated compounds previously described. Each compound in the left-hand column of the table may be produced by the action of chlorine on either of the compounds which precede it.

*Chlorethylene* or *Chloride of Vinyl*,  $C^2H^4.Cl$ , is, at low temperatures, a very mobile liquid, boiling even at  $-18^\circ$  or  $-15^\circ$  C. The gas has an alliaceous odour, takes fire with difficulty, and burns with a red flame, green at the edges. Specific gravity of the gas = 2.166. In the liquid state it is insoluble in water, but dissolves in all proportions in alcohol and ether. Potassium slightly heated decomposes the gas, eliminating carbon and a small quantity of naphthalin. By chlorine in sunshine, and by perchloride of antimony, it is converted into the following compound:—

*Chloride of Chlorethylene*.  $C^2H^4.Cl^2 = C^2H^4.Cl.Cl^2$ .—The best mode of preparation is to pass the preceding gaseous compound into an apparatus containing pentachloride of antimony, and kept cool at the beginning of the action. It is an oily liquid, boiling at  $116^\circ$  C., and resembling Dutch liquid in appearance and in odour. Specific gravity = 1.422 at  $17^\circ$  C. Vapour-density, observed = 4.722—4.672; calculated (2 vol.) = 4.691.

*Dichlorethylene*.  $C^2H^4.Cl^2$ .—Very volatile liquid boiling between  $36^\circ$  and  $40^\circ$  C. Odour alliaceous, like that of monochlorethylene. Specific gravity = 1.250 at  $16^\circ$  C. Vapour-density, observed = 3.321, calculated (2 vol.) = 3.36. When kept in sealed tubes, it changes spontaneously into a white crystalline isomeric substance. If poured into chlorine gas in sunshine, it takes fire and deposits carbon; but if poured into the chlorine in the shade, left there for 12 hours, and then exposed to the sun, it is completely converted into crystals of perchlorinated chloride of ethylene, or sesquichloride of carbon,  $C^2Cl^4.Cl^2$ .

*Chloride of Dichlorethylene*.  $C^2H^4.Cl^3 = C^2H^4.Cl^2.Cl^2$ .—Produced by the continued action of chlorine on Dutch liquid or on chloride of chlorethylene. It is a liquid smelling like the preceding compounds. Specific gravity = 1.676 at  $19^\circ$  C. Boiling point  $136^\circ$  C. Vapour-density, observed = 5.796, calculated (2 vol.) = 5.821.

*Trichlorethylene*.  $C^2H^4.Cl^3$ .—Produced by the action of alcoholic potash on the preceding. It is an oily liquid which gives off hydrochloric acid when distilled.

*Chloride of Trichlorethylene*.  $C^2H^4.Cl^4 = C^2H^4.Cl^3.Cl^2$ .—Produced by the action of chlorine on Dutch liquid. It is liquid at  $0^\circ$  C., has a rather fragrant odour and hot sweetish taste. Specific gravity = 1.66267 at  $0^\circ$  C. Boiling point,  $153.8^\circ$  under a pressure of 763.35 mm. Vapour-density, observed = 7.087, calculated (2 vol.) = 7.016. Alcoholic potash decomposes it, with great rise of temperature, yielding chloride of potassium and the following compound:—

*Perchlorethylene* or *Dichloride of Carbon*.  $C^2Cl^4$ .—Produced also by several other reactions (i. 767).

*Chloride of Perchlorethylene* or *Trichloride of Carbon*.  $C^2Cl^4 = C^2Cl^4.Cl^2$ .—Produced by the continued action of chlorine on chloride of ethylene or its chlorinated derivatives, and by several other reactions (i. 766).



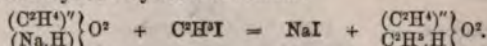
**ETHYLENE, CHLORIODIDE OF.**  $C^2H^4Cl$ . (Maxwell Simpson, Proc. Roy. Soc. xi. 590; xii. 278).—Produced by passing ethylene-gas into aqueous chloride of iodine, or by agitating iodide of ethylene with the same solution containing free iodine; the former process is to be preferred. The reddish oil which collects at the bottom of the liquid is washed with dilute potash and distilled.

Chloriodide of ethylene is a colourless oil having a sweet taste and slightly soluble in water. Specific gravity = 2.151 at  $0^\circ C$ . Boils at  $145^\circ$ — $147^\circ C$ . Heated with alcoholic potash, it decomposes, yielding iodide of potassium and a gas which burns with a green flame, and is probably chloride of vinyl,  $C^2H^3Cl$ .

**ETHYLENE, CYANIDE OF.**  $C^2H^4N^2 = C^2H^4.Cy^2$ .—Obtained by the action of cyanide of potassium on bromide or chloride of ethylene (see p. 212).

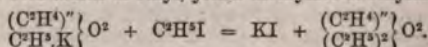
**ETHYLENE, DIBROMIDE, DICHLORIDE, and DI-IODIDE OF.** See ETHYLENE, BROMIDE, CHLORIDE, and IODIDE OF.

**ETHYLENE, ETHERATES OF.** (Wurtz, Ann. Ch. Pharm. cviii. 84).—The *monoethylate* or *ethyl-glycol*,  $C^2H^4O^2 = \frac{(C^2H^4)^n}{C^2H^3.H} O^2$ , is produced by the action of iodide of ethyl on ethylate of sodium:



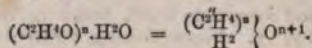
It is an ethereal liquid, boiling somewhere about  $130^\circ C$ ., but it has not been obtained quite free from the following compound.

*Diethylate of Ethylene, or Diethyl-glycol.*  $C^4H^{10}O^2 = \frac{(C^2H^4)^n}{(C^2H^3)^2} O^2$ .—The preceding compound treated with potassium yields the compound  $\frac{(C^2H^4)^n}{C^2H^3.K} O^2$ ; and this, when treated with iodide of ethyl, yields diethylate of ethylene:



It is a colourless, very mobile liquid, having a fragrant ethereal odour. Specific gravity = 0.7993 at  $0^\circ C$ . Boils at  $123.5^\circ$  under a pressure of 758.8 mm. Vapour-density, obs. = 4.095; calc. = 4.089. It is isomeric with acetal, but is distinguished therefrom by its higher boiling-point, acetal boiling at  $104^\circ C$ .

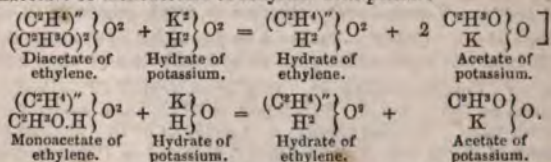
**ETHYLENE, HYDRATES OF.—ETHYLENIC ALCOHOLS.** These bodies, which may be regarded as compounds of oxide of ethylene and water, are represented by the general formula:



The first term of the series ( $n = 1$ ) was discovered by Wurtz in 1856; the rest, up to  $n = 6$ , were obtained by Wurtz and by Lourenço in 1859 and 1860.

**Monoethylenic Alcohol, Glycol.**  $C^2H^4O^2 = \frac{(C^2H^4)^n}{H^2} O^2 = C^2H^4O.H^2O$ . (Wurtz, Compt. rend. xliii. 199; Ann. Ch. Pharm. c. 110; further, and in detail, Ann. Ch. Phys. [3] lv. 400; Ann. Ch. Pharm. Suppl. i. 85).—The term *glycol*, formed from the first syllable of *glycerin* and the last of *alcohol*, denotes that the compound, as a diatomic alcohol, is intermediate between alcohol and glycerin, which are respectively mono- and tri-atomic.

*Preparation.*—This compound, the type of the diatomic alcohols, is obtained by distilling the diacetate or monoacetate of ethylene with potash:



1. Diacetate of ethylene (6.15) grm. is mixed in a flask with hydrate of potassium (4.72 grm.), previously ignited and pulverised. A brisk action immediately takes place, and after the lapse of a day, a mass of acetate of potassium is found in the flask. The mixture is then heated to  $180^\circ C$ . in an oil-bath, and after a small distillation-tube has been adapted to the flask, the heat is raised to between  $250^\circ$  and  $260^\circ$ . A colourless liquid then passes over, which is to be rectified, and the portion which distils between  $190^\circ$  and  $200^\circ$  collected apart. (Wurtz.)

2. Atkinson (Phil. Mag. [4] xvi. 433) prepares glycol by the action of potash or baryta on *monoacetate of ethylene*, p. 668. According to Debus (Ann. Ch. Pharm. cx. 316), the quantity of glycol thus obtained is only about half the calculated quantity, the loss apparently arising from the formation of a compound which is but slowly resolved by heat into glycol and acetate of potassium. He therefore recommends the following process:—

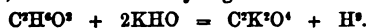
3. The monoacetate of ethylene mixed with an equal volume of water is exposed for twelve or sixteen hours in a strong, well-corked flask, to the temperature of boiling water, whereby it is for the most part resolved into acetic acid and glycol. On distilling the contents of the flask, water and acetic acid pass over below 150° C.; glycol mixed with a considerable quantity of the undecomposed acetate between 150° and 190°; and above 190°, glycol containing a comparatively small portion (about 15 per cent.) of the acetate. The portion boiling between 150° and 190° is again heated with water in a close vessel; the portion of the product which distils above 190° is mixed with the former portion boiling at that temperature; the whole is distilled with a quantity of solid potash, just sufficient to neutralise the acetic acid; and the liquid which passes over at 245° is rectified. Glycol is thus obtained boiling at 196°.

In all processes for obtaining glycol from the acetates or other compounds of ethylene, excess of alkali is to be avoided, as it greatly diminishes the quantity of the product; in general, also, hydrate of barium is preferable to potash. The following method gives good results when rather large quantities of glycol are to be prepared. The mixture of mono- and diacetate of ethylene, boiling between 180° and 190°, which is obtained by the action of bromide of ethylene on acetate of potassium (pp. 566, 567), is mixed with as much hydrate of barium as would be sufficient to decompose it were it all pure mono-acetate of ethylene, and the mixture is heated in a water-bath till the alkaline reaction disappears; a further quantity of hydrate of barium is then added in small portions at once, the mixture being heated for an hour or more after each addition, until the alkaline reaction becomes permanent. The greater part of the acetate of barium thus formed crystallises out on cooling; the crystals are separated and washed with alcohol, the alcoholic washings being added to the liquid drained from the crystals, whereby more acetate of barium is precipitated; this is separated by filtration; and the filtrate then yields pure glycol by fractional distillation.

4. Glycol is also produced, together with diethylenic and a small quantity of triethylenic alcohol, by the direct combination of water with oxide of ethylene. When oxide of ethylene is heated with water for several days in a strong sealed flask, a sweetish liquid is obtained, from which glycol may be separated by fractional distillation. (Wurtz, Ann. Ch. Pharm. cxiii. 255.)

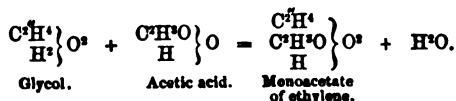
*Properties.*—Glycol is a colourless, inodorous, somewhat viscid liquid, of specific gravity 1.125, boiling at 197.5° C. It mixes with water and with alcohol, but is only slightly soluble in ether. It dissolves hydrate of potassium, chloride of calcium, chloride of sodium, chloride of zinc, trichloride of antimony, and mercuric chloride; carbonate of potassium in small quantity, the sulphate scarcely at all.

*Decompositions.*—1. Glycol is easily oxidable. When it is dropt on *platinum-black*, the metal becomes incandescent, and carbonic anhydride is given off. If the action be moderated by diluting the glycol with water, and the oxygen of the air with carbonic anhydride, glycolic acid, C<sup>2</sup>H<sup>4</sup>O<sup>3</sup>, is produced by the oxidation.—2. Dilute *nitric acid* at mean temperatures converts glycol into glycolic acid, at higher temperatures into oxalic acid (Wurtz). When glycol, diluted with four times its volume of water, is placed in a tall vessel, strong nitric acid poured in through a long tube-funnel, so as to form a layer at the bottom, and the whole heated to about 30° C., glycolic acid, glyoxylic acid, C<sup>2</sup>H<sup>3</sup>O<sup>3</sup>, and perhaps also glyoxal, C<sup>2</sup>H<sup>2</sup>O<sup>3</sup>, are formed (Debus, Ann. Ch. Pharm. cx. 316).—3. Glycol heated to 250° C. with *hydrate of potassium*, is converted into oxalic acid, with evolution of hydrogen:



4. Glycol heated with *chloride of zinc* is dehydrated, and yields aldehyde, C<sup>2</sup>H<sup>4</sup>O (isomeric with oxide of ethylene), and acetaldehyde, C<sup>2</sup>H<sup>4</sup>O<sup>2</sup>, a polymeric modification of aldehyde, boiling at 110° C. (Wurtz, Bauer, Rép. Chim. pure, 1860, p. 244).—

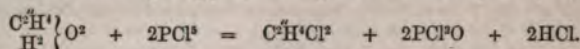
5. Glycol heated with *oxygen-acids* yields ethylenic ethers containing 1 or 2 at. of the acid radicle, according to the proportions used (Lourenço, Bull. Soc. Chim. Nov. 1859; Ann. Ch. Pharm. cxiv. 122), e. g.:



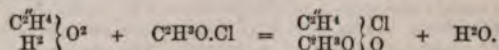
6. Heated with *hydrochloric acid*, it yields hydroxychloride of ethylene (glycolic chlorhydrin). (Wurtz.)



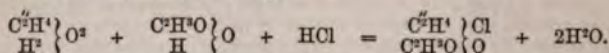
Similar reactions with *hydrobromic* and *hydriodic acids* (Wurtz).—7. *Pentachloride of phosphorus* acts violently on glycol, forming dichloride of ethylene (Wurtz):



8. Glycol is likewise strongly attacked by the *chlorides of acetyl, butyryl*, and other monatomic acid radicles, yielding acetoxychloride of ethylene, &c. (Lourenço, p. 670); thus:



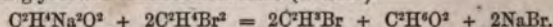
The same, and analogous compounds, are obtained by heating glycol with a fatty acid and hydrochloric or hydriodic acid: *e. g.*



9. Glycol heated with *iodide of ethyl* is partially decomposed, yielding monoethylate of ethylene (p. 676).

*Ethylenates of Sodium*.—Sodium acts rapidly on glycol, eliminating hydrogen and forming monosodic ethylenate or monosodic glycol,  $\begin{array}{c} \text{C}^{\text{H}^1} \\ \text{Na.H} \end{array} \left\{ \begin{array}{c} \text{O}^2 \\ \text{H}^2 \end{array} \right\} \text{O}^2$ , a white crystalline substance, which, when treated with iodide of ethyl, yields iodide of sodium and monoethylate of ethylene (p. 574). Heated in a sealed tube with bromethylene (bromide of vinyl),  $\text{C}^{\text{H}^3}\text{Br}$ , it yields ethylene gas and glycol, together with bromide of sodium and a small quantity of a sodium-salt which is soluble in alcohol, and when decomposed by sulphuric acid, yields an acid having the odour of acetic acid, but exerting a reducing action on silver-salts. (Wurtz.)

Monosodic ethylenate fused with excess of sodium is slowly converted into disodic ethylenate or disodic glycol,  $\text{C}^{\text{H}^1}.\text{Na}^2.\text{O}^2$ . This compound heated with dibromide of ethylene in a flask connected with a well cooled receiver, yields bromethylene, together with glycol and bromide of sodium (Wurtz):



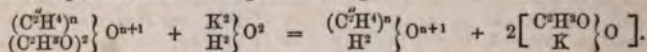
#### *Polyethylenic Alcohols.*

These compounds, whose composition is represented by the general formula given on p. 574, when  $n = 2$  or upwards, are produced in the following ways:

1. By heating oxide of ethylene with water in sealed tubes. In this manner Wurtz obtained diethylenic alcohol, together with monethylenic and a small quantity of triethylenic alcohol.

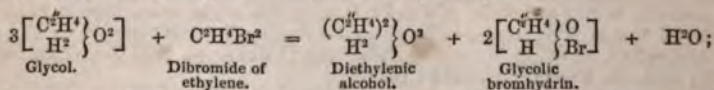
2. By heating oxide of ethylene with glycol in sealed tubes: this reaction yields diethylenic and triethylenic alcohols. (Wurtz.)

3. By distilling the corresponding polyethylenic diacetates (p. 568) with an alkali, the general equation of the decomposition being:

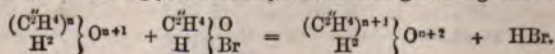


By this process, Wurtz obtained the di-, tri-, and tetr-ethylenic alcohols.

4. By heating glycol with dibromide of ethylene to  $110^\circ$ – $126^\circ$  C. in sealed tubes. The first products of the reaction are diethylenic alcohol, glycolic bromhydrin (hydroxybromide of ethylene), and water, as shown by the equation:



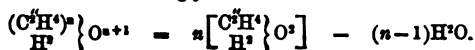
and the other polyethylenic alcohols are formed, each from the one next below it in the series, by the action of the glycolic bromhydrin, according to the general equation:





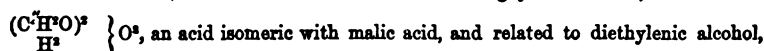
The hydrobromic acid thus formed then acts on the excess of glycol present, reproducing glycolic bromhydrin, and thus the action is continued. By this process, the 2-, 3-, 4-, 5-, and 6-ethylenic alcohols have been obtained, and separated by fractional distillation; and when a sufficient excess of glycol is present, the temperature being still kept between 110° and 120° C., still higher members of the series are obtained, becoming continually more viscid, and each differing from the preceding in boiling-point by about 45° C. If the temperature of the mixture is allowed to rise above 130°, the liquid turns brown and yields the hydrobromic ethers of the polyethylenic alcohols instead of the alcohols themselves, the hydrobromic acid produced by the reaction then acting, not only on the glycol, but likewise on the polyethylenic alcohols. (Lourenço, *Compt. rend. li.* 365; *Rép. Chim. pure, ii.* 467; *Ann. Ch. Pharm. cxvii.* 269.)

The polyethylenic alcohols may be supposed to be formed by the union of two or more molecules of glycol, with elimination of a number of molecules of water, less by one than the number of molecules of glycol which enter into the combination generally:



**Diethylenic Alcohol.**  $\text{C}^4\text{H}^8\text{O}^3 = \left\{ \begin{smallmatrix} \text{C}^2\text{H}^4 \\ \text{H}^2 \end{smallmatrix} \right\}^2 \text{O}^3 = (\text{C}^2\text{H}^4\text{O})^2.\text{H}^2\text{O}$ . (Lourenço, *Bull. Soc. Chim.* 1859, p. 77.)—This compound, the first discovered of the polyethylenic alcohols, contains the elements of 1 at. oxide of ethylene and 1 at. glycol,  $(\text{C}^2\text{H}^4\text{O} + \text{C}^2\text{H}^4\text{O})$ , and hence was originally called "intermediate glycol-ether." It is prepared by heating 3 at. glycol with 1 at. dibromide of ethylene (equal weights of the two) to 120° C. in a sealed flask for four days. Other modes of formation have already been mentioned.

It is a sweetish syrupy liquid, boiling at about 245°C., soluble in water, alcohol, and ether. Vapour-density, observed = 3.78 at 311°C.; calculated = 3.67 (Lourenço). It is easily oxidised by contact with platinum-black, or by treatment with nitric acid; the latter converts it into diglycolic acid,  $\text{C}^4\text{H}^6\text{O}^5 =$



$\left\{ \begin{smallmatrix} \text{C}^2\text{H}^4 \\ \text{H}^2 \end{smallmatrix} \right\}^2 \text{O}^5$ , in the same manner as glycolic acid,  $\left\{ \begin{smallmatrix} \text{C}^2\text{H}^2\text{O}^2 \\ \text{H} \end{smallmatrix} \right\} \text{O}^3$ , to glycol,  $\left\{ \begin{smallmatrix} \text{C}^2\text{H}^4 \\ \text{H}^2 \end{smallmatrix} \right\} \text{O}^2$ , both these acids containing the diatomic radicle glycolyl,  $\text{C}^2\text{H}^2\text{O}$ , derived from ethylene,  $\text{C}^2\text{H}^4$ , in the same manner as acetyl,  $\text{C}^2\text{H}^3\text{O}$ , from ethyl,  $\text{C}^2\text{H}^5$ ; viz. by the substitution of O for  $\text{H}^2$ . (Wurtz.)

**Triethylenic Alcohol.**  $\text{C}^6\text{H}^{12}\text{O}^4 = \left\{ \begin{smallmatrix} \text{C}^2\text{H}^4 \\ \text{H}^2 \end{smallmatrix} \right\}^3 \text{O}^4 = (\text{C}^2\text{H}^4\text{O})^3.\text{H}^2\text{O}$ .—This compound is best prepared by heating oxide of ethylene with glycol in a sealed tube  $(2\text{C}^2\text{H}^4\text{O} + \text{C}^2\text{H}^4\text{O}^2 = \text{C}^6\text{H}^{12}\text{O}^4)$ . The chief product of this reaction is, however, diethylenic alcohol; but after this has been removed by fractional distillation, the residue yields at about 290° C. a very thick liquid, which is triethylenic alcohol. (Wurtz.)

This alcohol is likewise easily oxidised by platinum-black and by nitric acid, the latter converting it into diglycolethylenic acid,  $\text{C}^6\text{H}^{10}\text{O}^6 = \left\{ \begin{smallmatrix} \text{C}^2\text{H}^4 \\ \text{H}^2 \end{smallmatrix} \right\}^2 (\text{C}^2\text{H}^2\text{O}^2)^2 \text{O}^2$ . (Wurtz.)

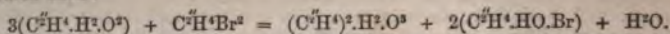
**Tetreethylenic Alcohol.**  $\text{C}^8\text{H}^{16}\text{O}^5 = \left\{ \begin{smallmatrix} \text{C}^2\text{H}^4 \\ \text{H}^2 \end{smallmatrix} \right\}^4 \text{O}^5 = (\text{C}^2\text{H}^4\text{O})^4.\text{H}^2\text{O}$ .—Boils under the ordinary pressure, above 300° C.; in a highly rarefied atmosphere (under a pressure of 0.025 mm.) at 230° C. (Lourenço.)

**Pentethylenic Alcohol.**  $\text{C}^{10}\text{H}^{20}\text{O}^6 = \left\{ \begin{smallmatrix} \text{C}^2\text{H}^4 \\ \text{H}^2 \end{smallmatrix} \right\}^5 \text{O}^6 = (\text{C}^2\text{H}^4\text{O})^5.\text{H}^2\text{O}$ .—Boils at 230° under a pressure of 0.025 mm. (Lourenço.)

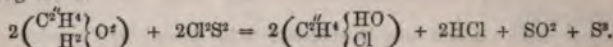
**Hexethylenic Alcohol.**  $\text{C}^{12}\text{H}^{24}\text{O}^7 = \left\{ \begin{smallmatrix} \text{C}^2\text{H}^4 \\ \text{H}^2 \end{smallmatrix} \right\}^6 \text{O}^7 = (\text{C}^2\text{H}^4\text{O})^6.\text{H}^2\text{O}$ .—Boils at 325° under the same pressure. (Lourenço.)

**ETHYLENE, HYDROXYBROMIDE OF.**  $\text{C}^2\text{H}^4\text{BrO} = (\text{C}^2\text{H}^4)^{\cdot}\text{HO.Br}$ . *Glycolic Bromhydrin, Glycol bromhydrique*. (Lourenço, *Bull. Soc. Chim. de Paris, i.* 77.)—Produced, together with diethylenic alcohol, by heating 3 at. monethylenic

alcohol (glycol), with 1 at. bromide of ethylene (equal weights of the two), to  $120^{\circ}\text{C}$ . in a sealed flask:



**ETHYLENE, HYDROXYCHLORIDE OF.**  $\text{C}^2\text{H}^4\text{ClO} = (\text{C}^2\text{H}^4)^{\cdot}\text{HO}.\text{Cl}$ . *Glycolic Chlorhydrin, Glycol chlorhydrique.* (Wurtz, Ann. Ch. Pharm. cx. 125.) —Obtained: 1. By saturating glycol with hydrochloric acid gas, heating the liquid to  $100^{\circ}\text{C}$ ., repeating these operations till the liquid, on being removed from the tube, no longer gives off fumes of hydrochloric acid, and rectifying (Wurtz).—2. By heating glycol to  $100^{\circ}\text{C}$ . with disulphide of chlorine in a flask provided with an upright condensing tube:

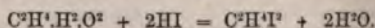


The sulphide of chlorine must be added at once in slight excess, otherwise an insoluble compound (perhaps a sulphurous ether) is produced at the same time. The heating is continued as long as any gas is evolved; the product is dissolved in ether; decanted from the sulphur which separates; then shaken up with moist carbonate of potassium, and distilled after the ether has been evaporated off over the water-bath. The product amounts to nearly the theoretical quantity. (Carius, Ann. Ch. Pharm. exxiv. 257.)

Hydroxychloride of ethylene is a colourless neutral liquid, boiling at  $128^{\circ}\text{C}$ ., soluble in water, burning with green colour in the flame of a lamp (Wurtz). Diluted with half its volume of water, and treated with *sodium-amalgam*, it is converted into common alcohol,  $\text{C}^2\text{H}^6\text{O}$ , the change consisting in the replacement of an atom of chlorine by an atom of hydrogen (Lourenço, Compt. rend. lii. 1043). Treated with an alcoholic solution of *sulphydrate of potassium*, it yields oxysulphydrate of ethylene,  $\text{C}^2\text{H}^4.\text{H}^2.\text{SO}$ . (Carius.)

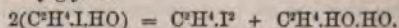
**ETHYLENE, HYDROXYIODIDE OF.**  $\text{C}^2\text{H}^4\text{IO} = (\text{C}^2\text{H}^4)^{\cdot}\text{HO}.\text{I}$ . *Glycolic Iodhydrin, Glycol iodhydrique.* (Maxwell Simpson, Proc. Roy. Soc. x. 1191.)

—Hydriodic acid is rapidly absorbed by glycol, great heat being evolved, and the liquid becoming black and thick from separation of iodine; and on removing the iodine by dilute potash, a mass of white crystals is obtained, consisting of iodide of ethylene:



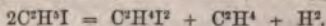
But if the temperature be prevented from rising by surrounding the vessel with cold water during the passage of the gas, a liquid product is obtained, which, after being treated with metallic silver to remove free iodine, exhibits approximately the composition of glycolic iodhydrin, viz. 11.1 per cent. carbon and 3.5 hydrogen, the formula  $\text{C}^2\text{H}^4\text{IO}$  requiring 13.9 C. and 3.0 H.

It is soluble in water and alcohol, but insoluble in ether. It has no taste at first, but almost burns the tongue after a time. It is decomposed by heat, yielding iodide of ethylene, and probably glycol:



It acts with great energy on silver-salts. Potash decomposes it, yielding iodide of potassium and oxide of ethylene.

**ETHYLENE, IODIDE OF.**  $\text{C}^2\text{H}^4\text{I}^2$ .—Discovered in 1821 by Faraday (Ann. Phil. xviii. 118); examined also by Regnault (Ann. Ch. Phys. lix. 367), D'Arcet (l'Institut. 1835, No. 105), and E. Kopp (J. Pharm. [3] vi. 110). It is produced: 1. By the direct combination of iodine and ethylene in sunshine (Faraday), or under the influence of a heat of  $50^{\circ}$ — $60^{\circ}\text{C}$ . (Regnault).—2. When vapour of iodide of ethyl is passed through a red-hot porcelain tube (E. Kopp):



3. By the action of hydriodic acid on glycol when the liquid is not kept cool (Simpson). It is easily prepared on the small scale by passing ethylene gas over gently heated iodine, part of the product then subliming in colourless needles. To obtain larger quantities, the iodine is heated in a long-necked flask, and a stream of ethylene gas directed on to its surface. The heat is raised very gradually, and as soon as the mass has become liquid, the gas is passed into it. By this means a brown liquid is at length obtained, which crystallises on cooling. It is purified from excess of iodine by washing with dilute potash, and finally recrystallised from alcohol. (Regnault.)

Iodide of ethylene crystallises in colourless needles or prisms, melts at  $75^{\circ}\text{C}$ ., and sublimes easily, but with partial decomposition; it is only in an atmosphere of hydrogen or ethylene gas that it can be sublimed in perfectly colourless crystals. It is

insoluble in *water*, but dissolves easily in *ether* and in boiling *alcohol*, from which it crystallises for the most part on cooling.

Iodide of ethylene is easily resolved into ethylene and iodine, this decomposition taking place slowly, even at ordinary temperatures, especially under the influence of light. At 85° C. it takes place rapidly, either in the air or in *vacuo*. It burns when held in the flame of a spirit-lamp, giving off vapours of iodine and hydriodic acid. Chlorine or bromine converts the compound into chloride or bromide of ethylene, the iodine being partly set free, partly uniting with the chlorine or the bromine. Aqueous potash acts but slowly upon it, even at the boiling heat; but when boiled with alcoholic potash, it is completely decomposed, partly into ethylene and iodine, partly into hydriodic acid and iodethylene,  $C^2H^2I$ .

**ETHYLENE, IODATED.**  $C^2H^2I$ . *Iodethylene, Iodide of Vinyl*.—Prepared by distilling iodide of ethylene with a strong alcoholic solution of potash, the receiver being kept at a low temperature. On adding water to the distillate, iodethylene separates as a colourless liquid, having an alliacious odour. It is insoluble in water, but very soluble in alcohol and ether. Nitric acid decomposes it, separating iodine and red vapours. (Regnault, *loc. cit.*—E. Kopp, *Compt. rend.* xviii. 871.)

**ETHYLENE, IODOCHLORIDE OF.**  $C^2H^2ClI$ .—Obtained by agitating an aqueous solution of chloride of iodine containing a trace of free iodine with iodide of ethylene, till the latter is converted into a black oily liquid, washing this liquid with dilute potash, and distilling:



It is a colourless liquid having a sweet taste, slightly soluble in water, boiling at about 147° C. (Maxwell Simpson, *Proc. Roy. Soc.* xi. 390; *Rép. Chim. pure*, 1862, p. 350.)

**ETHYLENE, OXIDE OF.**  $C^2H^2O$ . *Ethylene ether, Glycolic ether*. (Wurtz [1869], *Compt. rend.* xlviii. 101; *Ann. Ch. Pharm.* cx. 125; *Rép. Chim. pure*, i. 222; in detail; *Ann. Ch. Phys.* [3] lv. 418, 427; *Compt. rend.* xlix. 398; *Ann. Ch. Pharm.* cxiv. 51; *Compt. rend.* l. 1195; *Ann. Ch. Pharm.* cxvi. 249; *Rép. Chim. pure*, ii. 340; *Compt. rend.* liii. 378; *liv.* 277; *Rép. Chim. pure*, 1862, p. 16, 176; *Chem. Soc. J.* xv. 387.)

This compound is produced by the action of potash on glycolic chlorhydrin. Chloride of potassium then separates, and oxide of ethylene is given off in vapour, which may be condensed in a receiver surrounded with a frigorific mixture and containing a few lumps of chloride of calcium, over which the product may be afterwards rectified.

Oxide of ethylene is a transparent colourless liquid, boiling at 13.5° C., under a pressure of 746.5 mm. Vapour-density, obs. = 1.422; calc. =  $1.525 \left( = \frac{2.12 + 4.1 + 16}{2} \times 0.0693 \right)$ . It is isomeric with aldehyde, but is distinguished from that compound by its boiling-point (aldehyde boiling at 21° C.), and by its strong basic properties. It does not unite with the acid sulphites of alkali-metals, and does not form with ammonia a compound analogous to aldehyde-ammonia (i. 107).

Oxide of ethylene mixes in all proportions with *water* and with *alcohol*. The aqueous solution treated with *sodium-amalgam* in a vessel cooled by a freezing mixture yields ethylic alcohol:



The liquid remaining after the alcohol has been distilled off contains glycol and the polyethylenic alcohols. (Wurtz, *Rép. Chim. pure*, 1862, p. 177.)

Oxide of ethylene is a strong base, uniting directly with acids, *e. g.* with *hydrochloric acid* to form hydroxychloride of ethylene or glycolic chlorhydrin (p. 577),  $C^2H^2O.HCl$ ; with *acetic acid* to form monoacetate of ethylene,  $C^2H^2O.C^2H^3O^2$ ; with *acetic anhydride* in various proportions, forming diacetate of ethylene,  $C^2H^2O.C^2H^3O^2$ , and the several polyethylenic diacetates included in the general formula,  $(C^2H^2O)^n.C^2H^3O^2 =$

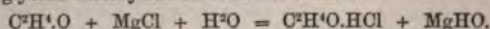
$\left. \begin{matrix} (C^2H^2O)^n \\ (C^2H^2O)^n \end{matrix} \right\} O^{n+1}$  (p. 568). In like manner it unites with *water*, forming glycol,

$C^2H^2O.H^2O$ , and the polyethylenic alcohols,  $(C^2H^2O)^n.H^2O = \left. \begin{matrix} (C^2H^2O)^n \\ H^2 \end{matrix} \right\} O^{n+1}$  (p. 574), which may also be regarded as compounds of oxide of ethylene with glycol,  $= \left. \begin{matrix} C^2H^2O \\ H^2 \end{matrix} \right\} O^2.(C^2H^2O)^{n-1}$ .

Oxide of ethylene precipitates *magnesia*, *alumina*, *ferric oxide*, and *cupric oxide*, as



hydrates, from the solutions of their salts, and is itself precipitated by *potash* or *lime* from its combination with hydrochloric acid. When it is sealed up in a flask with a strong solution of *chloride of magnesium* for several hours, hydrate of magnesium is deposited, and glycolic chlorhydrin remains in solution:



Oxide of ethylene unites directly with *water*, forming glycol and the polyethylenic alcohols (Wurtz); with *sulphydic acid*, forming (probably) sulphydic glycol and the polyethylenic oxysulphhydrates (Foster, p. 582); with *bromine*, forming the compound  $(\text{C}^2\text{H}^4\text{O})^2.\text{Br}^2$ ; with *ammonia*, to form the ethylene-hydoramines,  $(\text{C}^2\text{H}^4\text{O})^2.\text{NH}^2$  (p. 593); with *aldehyde*, forming the polymeric compound,  $\text{C}^2\text{H}^4\text{O}^2$ .—Oxide of ethylene vapour is absorbed by *chloride of calcium* at common temperatures. (Foster.)

*Compounds polymeric with Oxide of Ethylene.*

**Dioxethylene.**  $\text{C}^2\text{H}^4\text{O}^2 = \begin{matrix} \text{C}^2\text{H}^4 \\ \text{C}^2\text{H}^4 \end{matrix} \text{O}^2$ .—Bromide of ethylenic oxide subjected to the action of reducing agents, such as sulphydic acid or metals, gives up its bromine, and is converted into this compound. The reduction is best effected with mercury. On leaving this metal in contact with the bromine-compound in a tube for twenty-four hours, a colourless mass is obtained, consisting of bromide of mercury impregnated with a volatile liquid, which may be distilled off.

This liquid has a faint but pleasant odour, crystallises at  $90^\circ \text{C}.$ , boils at  $102^\circ$ . Specific gravity 1.0482. Vapour-density, obs. = 3.10; calc. (2 vol.) = 3.047 ( $= \frac{4.12 + 8.1 + 2.16}{2} \times 0.0693$ ). It is soluble in alcohol and ether; is not attacked by ammonia; unites slowly with acetic anhydride at  $120^\circ \text{C}.$

Dioxyethylene is probably the ether of diethylenic alcohol,  $(\text{C}^2\text{H}^4\text{O})^2.\text{H}^2\text{O} - \text{H}^2\text{O} = \text{C}^2\text{H}^4\text{O}^2$ ; it is perhaps also a homologue of Battlerow's dioxymethylene, produced by the action of oxide of lead or oxide of silver on iodide of methylene.

**Compound of Ethylenic Oxide with Aldehyde.**  $\text{C}^2\text{H}^4\text{O}^2 = \text{C}^2\text{H}^4\text{O}.\text{C}^2\text{H}^4\text{O}.$  (Wurtz, Rép. Chim. pure, 1862, p. 16.)—Obtained by heating aldehyde to  $100^\circ \text{C}.$  for a week with excess of glycol, and submitting the liquid product to fractional distillation. The compound  $\text{C}^2\text{H}^4\text{O}^2$  then passes over below  $100^\circ$ , afterwards water and glycol.

The compound of ethylenic oxide and aldehyde is a colourless liquid, having an agreeable, but rather pungent odour, somewhat like that of aldehyde. Specific gravity = 1.0002 at  $0^\circ \text{C}.$  Boils at  $82.5$ . Vapour-density, obs. = 3.192; calc. (2 vol.) = 3.047. If aldehyde is the oxide of ethylidene, this body may be regarded as an oxide of ethylene and ethylidene.

It is soluble in  $1\frac{1}{2}$  volumes of water, but is separated from the solution by potash and by chloride of calcium. Nitric acid attacks it strongly, forming glycollic and oxalic acids, together with other products. It is not altered by *caustic potash*. It reduces an ammoniacal solution of *nitrate of silver* at  $100^\circ \text{C}.$ , but not completely. Heated to  $140^\circ$  with *acetic acid*, it yields diacetate of ethylene, together with a much more volatile product, having an odour like that of Bauer's acetaldehyde.

Oxide of ethylene and aldehyde do not unite directly when heated together to  $100^\circ \text{C}.$ ; but the aldehyde is resinified as when heated with potash.

**ETHYLENE, OXYBROMIDE OF, or Bromide of Ethylenic Oxide.**

$\begin{matrix} \text{C}^2\text{H}^4\text{O} \\ \text{C}^2\text{H}^4\text{O} \end{matrix} \text{Br}^2$ .—When equivalent quantities of cooled bromine and oxide of ethylene are mixed and enclosed in a sealed tube immersed in a freezing mixture, the two bodies unite into a red crystalline compound, which melts at  $65^\circ \text{C}.$  to a dark red liquid, boiling at  $95^\circ$ , and emitting an orange-coloured vapour, which condenses on cooling to the red liquid and crystals. The compound has a pungent odour, and gives off a perceptible vapour at ordinary temperatures. It is insoluble in *water*, but soluble in *alcohol* and *ether*. Reducing agents, such as *metals* and *sulphydic acid*, remove the bromine and convert the compound into dioxethylene.

**ETHYLENE, OXYSULPHIDE OF.**  $\text{C}^2\text{H}^4\text{SO}$  (Crafts, Ann. Ch. Pharm. cxiv. 113; cxv. 123).—Produced: 1. By the action of water on sulphobromide of ethylene.—2. By the action of nitric acid on protosulphide of ethylene (p. 583). To obtain it pure, the sulphide of ethylene is added by small portions to fuming nitric acid; the excess of acid is then evaporated, and the crystalline residue is washed, first with water, then with alcohol, till it no longer exhibits any acid reaction. It is soluble in water, and crystallises from the solution in acute rhombohedrons of  $73^\circ$ . It does not unite with acids, is not attacked by ammonia, but potash decomposes it, separating sulphide of ethylene and a brown resinous body.

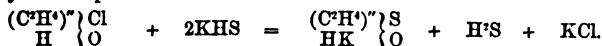
This body might be represented by the formula  $\begin{smallmatrix} \text{C}^{\text{H}}\text{H}^{\text{S}} \\ \text{H} \end{smallmatrix} \text{O}$ , or  $\begin{smallmatrix} \text{C}^{\text{H}}\text{H}^{\text{O}} \\ \text{H} \end{smallmatrix} \text{S}$ ; but its reactions are not such as to lead to the supposition that it is thus constituted.

**Dioxysulphide of Ethylene.**  $\text{C}^{\text{H}}\text{H}^{\text{S}}\text{O}^2$ . (Crafts, *loc. cit.*)—This compound, which has the composition of hydrate of sulphethylene,  $\begin{smallmatrix} \text{C}^{\text{H}}\text{H}^{\text{S}} \\ \text{H} \end{smallmatrix} \text{O}^2$ , or glycol in which 2 at. H are replaced by 1 at. S, or of glycolic acid in which O is replaced by S, is obtained by heating protosulphide of ethylene with fuming nitric acid in sealed tubes to  $150^{\circ}\text{C}$ , care being taken not to exceed this temperature, and to stop the operation before the oxidation is quite complete. As soon as the liquid in the tubes becomes well saturated with pernitric oxide, the dioxysulphide separates in small crystals. The tubes are then to be opened, and the liquid poured into water, which separates a small quantity of the dioxysulphide; and this, together with the crystals, is washed with boiling water, which removes the oxysulphide,  $\text{C}^{\text{H}}\text{H}^{\text{S}}\text{O}$ , that may adhere to them. Further purification may be effected by dissolving the crystals in strong nitric acid, and again separating with water.

Dioxysulphide of ethylene separates from its solution in strong nitric acid in small crystals, which under the microscope exhibit the form of prisms with obtuse summits. It is very slightly soluble in ordinary nitric acid, quite insoluble in water. Caustic potash dissolves it without blackening, but converts it into a body which appears to possess slight acid properties and is not precipitated from its solution by acids.

Guthrie (Chem. Soc. Qu. J. xiv. 132) obtained a hydrate of oxydisulphide of ethylene,  $\text{C}^{\text{H}}\text{H}^{\text{S}}\text{O} \cdot \text{H}^{\text{O}}$ , by treating sulphochloride of ethylene (p. 584) with caustic potash. It is a yellowish liquid, insoluble in water, soluble in alcohol and ether.

**ETHYLENE, OXYSULPHYDRATE OF.**  $\text{C}^{\text{H}}\text{H}^{\text{S}}\text{O} = \begin{smallmatrix} (\text{C}^{\text{H}}\text{H}^{\text{O}}) \\ \text{H} \end{smallmatrix} \text{S}$ . *Mono-sulphydrate of Ethylene. Sulphydic Glycol.* (Carius, Ann. Ch. Pharm. cxxiv. 267.)—This body, intermediate in composition between glycol and sulphydrate of ethylene (p. 585), is obtained as a potassium-salt by treating glycolic chlorhydrin with excess of sulphydrate of potassium in alcoholic solution:



The alcoholic liquid is boiled for a quarter of an hour in a vessel provided with an upright condensing tube; the liquid filtered from the chloride of potassium is supersaturated with dilute hydrochloric acid and evaporated in a shallow dish at  $30^{\circ}$ — $40^{\circ}\text{C}$ , till an oily liquid begins to separate; and the residue is treated with cold water, which dissolves chloride of potassium, and separates oxysulphydrate of ethylene, as an oily liquid, which is to be washed with a little cold water, dissolved in a small quantity of dilute alcohol; and the solution filtered, if necessary, and evaporated in a rarefied atmosphere, taking care to avoid over-heating.

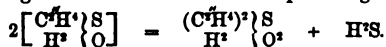
Oxysulphydrate of ethylene is a colourless liquid of the consistence of glycol, heavier than water, and having a faint odour like that of mercaptan. It dissolves sparingly in pure water, easily in water containing a small quantity of alcohol, very slightly in pure ether.

Nitric acid converts it almost wholly into isethionic acid,  $\text{C}^{\text{H}}\text{H}^{\text{S}}\text{O}^4$ , with only traces of sulphuric and oxalic acids.

With the salts of the heavy metals, oxysulphydrate of ethylene yields precipitates whose composition is expressed by the general formula  $\begin{smallmatrix} (\text{C}^{\text{H}}\text{H}^{\text{O}}) \\ \text{HM} \end{smallmatrix} \text{S}$ . These precipitates are flocculent, but quickly become granular, especially the lead-, mercury-, and silver-compounds. At  $100^{\circ}\text{C}$  they soften to glutinous masses; the mercury-salt, however, melts to a viscid liquid. The mercury-salt is white, moderately soluble in strong alcohol, whence it separates by slow evaporation in long thread-like curved needles. The zinc-salt is white; the copper-salt dirty blue-green; the lead-salt light yellow; the silver-salt yellowish. They are all insoluble in water and in acids, moderately soluble in strong alcohol, and are decomposed by sulphydrate of potassium.

**Diethylenic Oxysulphydrate.**  $\text{C}^{\text{H}}\text{H}^{\text{S}}\text{O}^2 = \begin{smallmatrix} (\text{C}^{\text{H}}\text{H}^{\text{O}})^2 \\ \text{H} \end{smallmatrix} \text{S}$ . (Carius, *loc. cit.*)

—This compound, analogous to diethylenic alcohol, is produced, with evolution of sulphydic acid, by boiling the alcoholic solution of the preceding compound:



To prepare it, the alcoholic solution obtained in the preparation of the monoethylenic compound, after filtration from chloride of potassium and neutralisation with hydro-



chloric acid, is evaporated, with gentle ebullition, till the excess of the latter is expelled; the oily liquid which then separates solidifies on cooling to a white crystalline mass, generally enclosing a certain quantity of the monoethylenic oxysulphhydrate; it may be purified by washing with cold, very dilute alcohol, and recrystallisation from alcohol.

Diethylenic oxysulphhydrate crystallises from alcohol in groups of very slender microscopic needles; melts at  $60^{\circ}\text{C}$ .; is insoluble in water, but easily soluble in alcohol. The solution is precipitated by metallic salts, the precipitates resembling those formed by the monoethylenic compound in colour and other properties.

Diethylenic oxysulphhydrate is easily oxidised by dilute nitric acid, taking up 3 at.

oxygen, and forming an acid,  $(\text{SO})^n \left\{ \begin{smallmatrix} (\text{C}^2\text{H}^4)^2 \\ \text{H}^2 \end{smallmatrix} \right\} \text{O}^4$ , which is dibasic, and easily forms salts in

which both atoms of typic hydrogen are replaced by metals. The barium- and lead-salts are easily soluble, and crystallise indistinctly in microscopic laminae.

When oxide of ethylene is heated to  $100^{\circ}\text{C}$ . in a close vessel filled with sulphydric acid gas, the gas is rapidly absorbed, and a somewhat oily liquid is formed, which cannot be distilled under the ordinary atmospheric pressure: it boils without distilling to any perceptible extent, the thermometer gradually rising to  $300^{\circ}$  and the liquid turning brown. The first product of this reaction is in all probability oxysulphhydrate of ethylene, and the gradual rise of the boiling point seems to show that a number of polyethylenic sulphhydrates of continually increasing complexity are subsequently formed. (G. C. Foster, *Epistolary communication*.)

**ETHYLENE, STEARATE OF.**  $\text{C}^{18}\text{H}^{34}\text{O}^4 = \left\{ \begin{smallmatrix} (\text{C}^2\text{H}^4)^n \\ (\text{C}^{16}\text{H}^{30}\text{O})^2 \end{smallmatrix} \right\} \text{O}^2$ .—Obtained by decomposing stearate of silver with bromide of ethylene and treating the product with ether, &c., as in the preparation of the benzoate (p. 568). It forms small, light, shining scales, resembling stearin, which melt at  $76^{\circ}\text{C}$ . (Wurtz.)

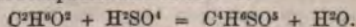
**ETHYLENE, SUCCINATES OF.** (Lourengo, *Rép. Chim. pure*, 1860, p. 179; *Ann. Ch. Pharm.* cxv. 368).—Two of these ethers have been obtained, viz.—

1. *Succinethylenic acid.*  $\text{C}^6\text{H}^{10}\text{O}^5 = \left\{ \begin{smallmatrix} (\text{C}^8\text{H}^4)^n \\ (\text{C}^4\text{H}^4\text{O}^2)^n \end{smallmatrix} \right\} \text{O}^2$ .—This compound, which

may be regarded as derived from diethylenic alcohol by the substitution of 1 at. succinyl for 1 at. ethylene, is produced when glycol and succinic acid in equivalent proportions are heated together in a sealed tube to  $190^{\circ}$ — $200^{\circ}\text{C}$ . for about ten hours. An oily acid liquid is then obtained, which on standing solidifies to a mass of small crystals of succinethylenic acid. This compound melts below  $100^{\circ}\text{C}$ ., is soluble in water and alcohol, sparingly in ether, and when neutralised with ammonia, forms with nitrate of silver a curdy precipitate insoluble in acids, and exhibiting a composition intermediate between  $\text{C}^6\text{H}^8\text{Ag}^2\text{O}^3$  and  $\text{C}^6\text{H}^8\text{AgO}^3$ , but nearer to the former.

2. *Neutral Succinate of Ethylene.*  $\text{C}^6\text{H}^8\text{O}^4 = \left\{ \begin{smallmatrix} (\text{C}^2\text{H}^4)^n \\ (\text{C}^4\text{H}^4\text{O}^2)^n \end{smallmatrix} \right\} \text{O}^2$ .—Obtained by heating succinethylenic acid to nearly  $300^{\circ}\text{C}$ . Water is then given off, and the residue solidifies on cooling to a crystalline mass of the neutral succinate. It melts below  $90^{\circ}\text{C}$ ., is insoluble in water and in ether, but moderately soluble in boiling alcohol, whence it separates on cooling in very small crystals. It is decomposed by distillation.

**ETHYLENE, SULPHATE (ACID) OF.**  $\text{C}^2\text{H}^4\text{SO}^5 = \left\{ \begin{smallmatrix} (\text{C}^2\text{H}^4)^n \\ (\text{SO}^2)^n \end{smallmatrix} \right\} \text{O}^2$ . *Sulphoglycolic acid* (Simpson, *Proc. Roy. Soc.* ix. 725).—Produced by heating a mixture of glycol and monohydrated sulphuric acid to  $160^{\circ}\text{C}$ .



It is not known in the free state. The barium-salt is obtained by diluting the above-mentioned mixture with water, saturating with carbonate of barium, filtering, and evaporating to a syrup over the water-bath, whereupon it separates as a white solid mass, which may be purified by pressure between paper, and evaporation in vacuo over oil of vitriol. It is somewhat deliquescent, and does not readily crystallise. Decomposes slightly at  $100^{\circ}\text{C}$ . Easily soluble, in water, nearly insoluble in absolute alcohol and in ether. From the aqueous solution sulphuric acid throws down sulphate of barium. Baryta-water occasions no precipitate in the cold, but on heating the liquid for some time, it becomes turbid, from separation of the same

**ENE, SULPHIDES OF.** These compounds are obtained by treating



chloride or bromide of ethylene with alcoholic solutions of the corresponding sulphides of potassium.

**Protosulphide of Ethylene.**  $C^2H^4S$ . Löwig and Weidmann in 1840 (Pogg. Ann. xlix. 123) obtained this compound in an impure state as an amorphous precipitate, decomposing when distilled, by the action of chloride of ethylene on protosulphide of potassium; and Crafts (Ann. Ch. Pharm. cxxiv. 110) has recently obtained it pure and in well-defined crystals, by the action of protosulphide of potassium on bromide of ethylene, which is much more easily attacked than the chloride. The action is attended with considerable rise of temperature, and the resulting sulphide of ethylene distilled off at  $200^\circ C$ . condenses in white crystals, which must be washed with ether to free them from an oily substance.

Protosulphide of ethylene is somewhat volatile at common temperatures, and distils undecomposed at  $199^\circ$  or  $200^\circ C$ ., solidifying at  $112^\circ$  in the crystalline form. It dissolves in alcohol, in ether, and more abundantly in sulphide of carbon, from which it separates in well-developed oblique rhombic prisms of  $69^\circ 44'$ , generally most developed in the direction of the base.

Chlorine decomposes it, with evolution of hydrochloric acid. With bromine it unites directly, forming a sulpho-bromide,  $C^2H^4SBr^2$ . It is oxidised by fuming nitric acid, the product consisting of  $C^2H^4SO$ , if the temperature is kept below  $100^\circ C$ ., but of  $C^2H^4SO^2$  (pp 580, 581), either pure or mixed with the preceding, if it is allowed to rise to  $150^\circ$  (Carius, Ann. Ch. Pharm. cxxv. 123). It does not unite with ammonia.

Protosulphide of ethylene is isomeric with the compound obtained by passing sulphydric acid into aldehyde. The latter compound is perhaps sulphide of ethyldene, and is distinguished by its higher boiling point, not beginning to distil below  $205^\circ C$ ., and the boiling point then quickly rising to  $260^\circ$ , at which temperature partial decomposition takes place. (Carius.)

**Disulphide of Ethylene,**  $C^2H^4S^2$ , is a soft yellowish powder, which melts below  $100^\circ C$ ., and is decomposed by distillation. (Löwig and Weidmann, Pogg. Ann. xlii. 84; xlix. 128; Gm. viii. 355.)

**Pentasulphide of Ethylene.**  $C^2H^4S^5$  (?).—Produced by the action of alcoholic tri-, or penta-sulphide of potassium on chloride of ethylene. It is a yellowish precipitate, melting below  $100^\circ C$ ., and decomposing at a somewhat higher temperature. (Löwig and Weidmann.)

**ETHYLENE, SULPHITES OF.** Isethionic acid,  $C^2H^4SO^4$ , may be regarded as *ethylene-monosulphurous acid*,  $C^2H^4O^2SO^2$ , that is, glycol with 1 at. sulphurous anhydride, or  $(C^2H^4)^{\frac{(SO^2)^n}{H^2}}O^3$ , diethylenic alcohol in which 1 at.  $C^2H^4$  is replaced by

$SO$ ; and disulphetholic acid,  $C^2H^4S^2O^4$ , may be regarded as *ethylene-disulphurous acid*,  $C^2H^4O^4.2SO^2$ , i. e. glycol with 2 at. sulphurous anhydride, or as  $(C^2H^4)^{\frac{(SO^2)^2}{H^2}}O^4$ ,

i. e. triethylenic alcohol in which 2 at.  $C^2H^4$  are replaced by 2 at.  $SO$  (Carius, Ann. Ch. Pharm. cxxiv. 262). See ISETHIONIC ACID, and SULPHUROUS ETHERS.

**ETHYLENE, SULPHOBROMIDE OF.**  $C^2H^4SBr^2$ . (Carius, Ann. Ch. Pharm. cxxiv. 113).—This compound, which may be regarded as a dibromide of ethylenic sulphide,  $C^2H^4S.Br^2$ , or as a sulphydrate of dibromethyl,  $(C^2H^4Br^2)^{\frac{H^2}{S}}$ , is produced by the direct combination of bromine with protosulphide of ethylene. It is a yellow solid substance, nearly insoluble in rectified ether and in sulphide of carbon. When exposed to moist air, or treated with a small quantity of water, it is converted into white crystals containing less bromine than the original compound. These crystals dissolve in a larger quantity of water; and by treating the solution with oxide of silver to remove hydrobromic acid, then filtering and evaporating, small rhombic tables are obtained, consisting of oxysulphide of ethylene,  $C^2H^4SO$ .

**ETHYLENE, SULPHOCHLORIDES OF.** (Guthrie, Chem. Soc. Qu. J. xii. 109; xiii. 35 and 134; xiv. 128.—Jahresber. d. Chem. 1849, p. 479; 1860, p. 433).—The following compounds of this group have been obtained:

Dichlorosulphide of Ethylene	or	Sulphydrate of Dichlorethyl,
$C^2H^4.Cl^2S$	=	$C^2H^4.Cl^2\left\{\begin{smallmatrix} S \\ H \end{smallmatrix}\right.$
Disulphochloride of Ethylene	or	Disulphide of Chlorethyl
$C^2H^4.Cl^2S^2$	=	$C^2H^4.Cl\left\{\begin{smallmatrix} S^2 \\ C^2H^4.Cl \end{smallmatrix}\right.$

Disulphochloride of Chloretylene	or	Disulphide of Dichloretethyl
$C^2H^4Cl^2.Cl^2S^2$	=	$\left. \begin{matrix} C^2H^4Cl^2 \\ C^2H^4Cl^2 \end{matrix} \right\} S^2$
Disulphochloride of Dichloretethylene	or	Disulphide of Trichloretethyl
$C^2H^4Cl^4.Cl^2S^2$	=	$\left. \begin{matrix} C^2H^4Cl^3 \\ C^2H^4Cl^3 \end{matrix} \right\} S^2$

The first two of these compounds are produced by the direct combination of the chlorides of sulphur,  $Cl^2S$  and  $ClS$ , with ethylene; the third is also a product of the action of  $ClS$  on ethylene; and the fourth is produced by the action of chlorine on the third, or on disulphide of ethyl.

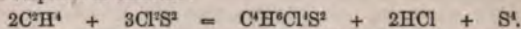
They are all decomposed by distillation, and therefore the weights of their molecules cannot be determined by experiment. The last compound may, however, be produced by the direct substitution of chlorine in disulphide of ethyl, which, as shown by its vapour-density (p. 547), is  $(C^2H^4)^2.S^2$ , not  $C^2H^4S$ ; the product formed from it by the action of chlorine is therefore  $(C^2H^4Cl^3)^2.S^2$ , not  $C^4H^8Cl^6S$ ; and hence also it is probable that the two preceding compounds are correctly represented by the formulæ above given, rather than by the halves of those formulæ.

*Dichlorosulphide of Ethylene*,  $C^2H^4Cl^2S$ , is obtained by passing ethylene gas very slowly through dichloride of sulphur ( $Cl^2S$ ) contained in a bulb-apparatus, and when the saturation is nearly finished, heating the liquid to  $100^\circ C.$ , and passing a rapid stream of ethylene through it, partly to complete the action, partly to get rid of chlorinated compounds of ethylene formed at the same time; or the liquid, before complete saturation, is dropped into water at  $80^\circ C.$  to decompose the still remaining chloride of sulphur; repeatedly shaken up with fresh quantities of water at the same temperature; then left in contact for some time with dilute soda-ley; agitated with anhydrous ether to free it from suspended sulphur; the residue left on evaporating the ether is again dissolved in the smallest possible quantity of ether; and the residue left on evaporating this solution is dried in vacuo over oil of vitriol. (Ann. Ch. Pharm. cxiii. 2.)\*

It is a straw-yellow liquid, having a pungent odour like that of oil of mustard, an astringent taste like that of horse-radish, and raising blisters on the skin; even the vapour destroys the epidermis on the more tender parts. Specific gravity 1.408 at  $13^\circ C.$  It is insoluble in water, nearly insoluble in cold, slightly soluble in hot alcohol, soluble in about 50 times its volume of boiling ether. It is decomposed by heat, giving off chlorine, sulphydric acid, and volatile products containing sulphur and carbon.

*Disulphochloride of Ethylene*,  $C^2H^4Cl^2S^2$ , or *Disulphide of Monochloretethyl*,  $\left. \begin{matrix} C^2H^4Cl \\ C^2H^4Cl \end{matrix} \right\} S^2$ .—This compound was first obtained by Niemann (Ann. Ch. Pharm. cxiii. 288), afterwards in a state of greater purity by Guthrie. It is produced when disulphide of chlorine,  $Cl^2S^2$ , is brought in contact with ethylene gas, either in sunshine or at a temperature of  $100^\circ C.$  It is purified by agitation with warm water, drying, digestion in ether, and evaporation of the ethereal solution in vacuo. It is a pale yellow liquid, having a not unpleasant odour, a sweet astringent taste, and acting strongly on the mucous membranes. Specific gravity = 1.346 at  $19^\circ C.$  Caustic potash converts it into hydrate of ethylenic oxysulphide,  $\left. \begin{matrix} C^2H^4 \\ C^2H^4 \end{matrix} \right\} S.O.H^2O$ . Not volatile without decomposition.

*Disulphochloride of Monochloretethylene*,  $C^2H^4Cl^2S^2 = C^2H^4Cl^2.Cl^2S^2$ , or *Disulphide of Dichloretethyl*,  $\left. \begin{matrix} C^2H^4Cl^2 \\ C^2H^4Cl^2 \end{matrix} \right\} S^2$ .—This body is also a product of the action of ethylene on sulphide of chlorine:



It is prepared by passing a rapid current of dry ethylene gas for some time through sulphide of chlorine contained in a capacious retort provided with a vertical condensing tube, afterwards heating the liquid in a smaller retort till the boiling point rises to  $180^\circ C.$  (whereupon hydrochloric acid escapes and scarcely anything but unaltered sulphide of chlorine distils over); decanting the liquid residue from the sulphur which separates on cooling; digesting it for some hours with water at  $80^\circ C.$ , then with dilute soda-ley; and dissolving it in ether, &c., as in the preparation of the compound  $C^2H^4Cl^2S$ . It is a clear pale yellow liquid of specific gravity 1.599 at  $11^\circ C.$ , having a sweet, astringent taste, and when recently prepared, an agreeable odour, resembling oil of peppermint and oil of lemon; three or four drops of it produce head-ache. It is

\* The dichloride of sulphur is prepared by saturating disulphide of chlorine ( $S^2Cl^2$ ) with dry chlorine at  $10^\circ C.$  and collecting the distillate from this product, which passes over between  $70^\circ$  and  $90^\circ C.$



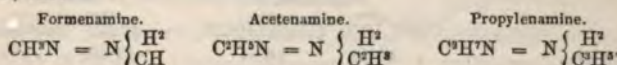
soluble in alcohol and ether, insoluble in water. Not volatile without decomposition. When treated with chlorine, it is converted into the following compound:—

*Sulphochloride of Dichlorethylene*,  $C^2H^4Cl^2S^2 = C^2H^4Cl^4Cl^2S^2$ , or *Disulphide of Trichlorethyl*,  $\left\{ \begin{smallmatrix} C^2H^2Cl^3 \\ C^2H^2Cl^3 \end{smallmatrix} \right\} S^2$ .—Produced by passing chlorine-gas through the preceding compound in the dark, first at mean temperature, afterwards at  $100^\circ C.$ , or by the action of chlorine on disulphide of ethyl. Purified by passing a stream of carbonic anhydride through it to remove hydrochloric acid and small quantities of sulphide of chlorine, then digesting in ether, &c. It is a clear, pale yellow liquid, of specific gravity 1.219—1.225 at  $13.5^\circ C.$  It has a pungent, suffocating odour, is insoluble in water, soluble in alcohol and ether; decomposes when distilled in the air, but volatilises completely without decomposition in an atmosphere of carbonic anhydride. (Guthrie.)

**ETHYLENE, SULPHYDRATE OF.**  $C^2H^4S^2 = \left\{ \begin{smallmatrix} C^2H^4 \\ H^2 \end{smallmatrix} \right\} S^2$ . *Ethylenic or Glycolic Mercaptan*.—Obtained in alcoholic solution by mixing chloride of ethylene with alcoholic sulphhydrate of potassium, and separating the liquid from the resulting chloride of potassium by distillation. The solution has a pungent odour like that of mercaptan, and forms with acetate of lead a yellow precipitate consisting of  $C^2H^4Pb^2S^2$ . (Löwig and Weidmann, Pogg. Ann. xlix. 132.)

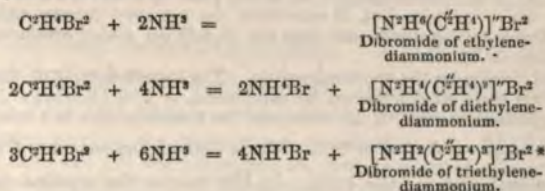
When bromide of ethylene is poured into a concentrated alcoholic solution of sulphhydrate of potassium, the liquid becomes warm, and deposits a large quantity of bromide of potassium; and on adding water to the filtered alcoholic solution, ethylenic mercaptan separates as a colourless oil, which is partially decomposed by distillation. (Kekulé, Lehrbuch, i. 655.)

**ETHYLENE-BASES.** Cloez in 1853 (l'Institut. 1853, p. 213), by heating alcoholic ammonia in sealed-tubes with chloride or bromide of ethylene, obtained three volatile bases, which he supposed to be monamines, containing the radicles  $CH$ ,  $C^2H^2$ , and  $C^3H^3$ , viz.:



The second of these bases, or a substance isomeric therewith, was likewise obtained by Natanson (Ann. Ch. Pharm. xcii. 48; xcvi. 20), who took the same view of its constitution.

But the more complete investigation to which these bases have been subjected by Hofmann (Proc. Roy. Soc. ix. 154; x. 224), has shown that they are diamines, formed from a double molecule of ammonia,  $N^2H^4$ , by the substitution of 1, 2, and 3 molecules of ethylene for 2, 4, and 6 at. of hydrogen respectively. The mode of formation of their hydrobromates, or the dibromides of the corresponding diammoniums, is shown by the following equations:—



The formation of these three diatomic bromides is precisely analogous to that of the monobromides of the ethylammoniums (p. 554), the first being produced by the simple combination of the ammonia with the ethylenic bromide, whereas the formation of the second and third is accompanied by that of bromide of ammonium.

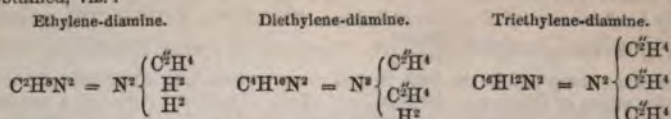
Chloride of ethylene appears to act on ammonia in a similar manner, but not so readily. The reaction presents, moreover, several phenomena which still require further investigation. The bromide acts upon alcoholic ammonia at ordinary temperatures, but on aqueous ammonia only when assisted by heat.

The dibromides of the ethylene-diammoniums distilled with potash yield the corresponding bases in the form of hydrates, which retain their water with such obstinacy that they can scarcely be dehydrated by caustic lime or baryta; the remark applies more especially to ethylene-diamine, which requires prolonged treatment with sodium

\* It deserves to be noticed that the experimental data which have reference to the formation and properties of the third base are still very scanty.—A. W. H.



to yield up the last portions of water. By this means the anhydrous bases or diamines are obtained, viz.:



The second of these formulæ is exactly double that of the acetamine of Cloez; the first and third differ from the double formulæ of formenamine and propylenamine (p. 585) by 2 at. hydrogen.

The inadmissibility of the monatomic formulæ is shown: *Firstly*, by the results of analysis, as may be seen by the following comparison of the calculated and experimental numbers of the hydrate of the first base ( $\text{C}^2\text{H}^6\text{N}^2.\text{H}^2\text{O}$ , or  $\text{C}^2\text{H}^8\text{N}^2.\text{H}^2\text{O}$ , according to Cloez;  $\text{C}^2\text{H}^6\text{N}^2.\text{H}^2\text{O}$  according to Hofmann), and of the corresponding hydrochlorate:

		<i>Hydrated Base.</i>			
		Calculation.		Analyses.	
		$\text{C}^2\text{H}^6\text{N}^2.\text{H}^2\text{O}$	$\text{C}^2\text{H}^8\text{N}^2.\text{H}^2\text{O}$	Cloez.	Hofmann.
Carbon . . .		31.58	30.76	31.12	30.67
Hydrogen . . .		10.52	12.82	12.78	12.97
Nitrogen . . .		36.84	35.90	35.80	36.32
Oxygen . . .		21.06	20.52		
		100.00	100.00		

		<i>Hydrochlorate.</i>			
		Calculation.		Analyses.	
		$\text{CH}^3\text{N}.\text{HCl}$	$\text{C}^2\text{H}^6\text{N}^2.\text{H}^2\text{Cl}^2$	Cloez.	Hofmann.
Carbon . . .		18.32	18.04	17.56	17.87
Hydrogen . . .		6.11	7.52	7.39	7.55
Nitrogen . . .		21.37	21.06	20.47	
Chlorine . . .		54.20	53.38	53.62	53.17
		100.00	100.00		

*Secondly*, by the boiling points. The three anhydrous bases boil at  $117^\circ$ , about  $170^\circ$ , and about  $210^\circ\text{C}$ . respectively, the difference of the first two being  $53^\circ$ , and of the second and third  $40^\circ$ . Now homologous substances related to one another in the manner indicated by the monatomic formulæ,  $\text{CH}^3\text{N}$ ,  $\text{C}^2\text{H}^6\text{N}$ ,  $\text{C}^3\text{H}^9\text{N}$ , that is to say, differing by  $\text{CH}^3$ , do not generally differ in boiling point by more than  $20^\circ$ . Moreover, methylamine, which contains 2 at. H more than the supposed formenamine of Cloez, is a gas at ordinary temperatures, and does not liquefy till cooled considerably below the freezing point of water.

*Thirdly*, and chiefly, by the vapour-densities. The vapour-density of the first base in the anhydrous state, as determined by experiment, is 2.00 (Hofmann): now the formula of ethylene-diamine,  $\text{C}^2\text{H}^6\text{N}^2$ , calculated for a condensation to 2 volumes, gives  $\frac{2 \cdot 12 + 8 \cdot 1 + 2 \cdot 14}{2} \times 0.0693 = 2.08$ , whereas that of formenamine,  $\text{CH}^3\text{N}$ , calculated for a like condensation, give 1.014. In like manner the vapour-density of the second anhydrous base is by experiment 2.7; and by calculation from the diatomic formula,  $\text{C}^4\text{H}^{10}\text{N}^2$ , representing a condensation to 2 volumes, it is 2.9, the monatomic formula,  $\text{C}^2\text{H}^6\text{N}$ , requiring 1.45.

The vapour-densities of the hydrated bases appear at first sight, to furnish an argument in favour of the monatomic formulæ. That of the first hydrated base was found by Cloez to be 1.47. Now the formula,  $\text{C}^2\text{H}^6\text{N}^2\text{O}$  or  $\text{C}^2\text{H}^8\text{N}^2\text{O}$ , calculated for 2 vol. gives  $\frac{2 \cdot 6 + 4 \cdot 1 + 14 + 8}{2} \times 0.0693 = 1.32$ ; whereas the diatomic formula,  $\text{C}^2\text{H}^{10}\text{N}^2\text{O}$  or  $\text{C}^4\text{H}^{10}\text{N}^2\text{O}^2$ , requires 2.70. This, however, is a case of *dis-association* (see *Atomic Weights*, i. 467), the hydrate splitting up, at the high temperature at which the vapour-density was taken, into water and the anhydrous base, each of which occupies 2 vols., and therefore the whole 4 vols. That these hydrated bases do actually split up in this manner at high temperatures, has been experimentally demonstrated with regard to another base of similar constitution, which will be afterwards mentioned (see p. 588).

The ethylene-diamines obtained as above are volatile, strongly alkaline bodies, which neutralise acids completely. Ethylene-diamine is a liquid; diethylene-diamine is a solid substance, crystallising in transparent, well-developed crystals, which, in winter are apt to attain considerable magnitude. Monethylene-diamine heated with *nitrous acid* yields oxide of ethylene and free nitrogen:



Assuming that the diatomic ethylene-bases imitate the deportment of the monatomic ethyl-bases, each of the ethylene-diamines, when treated with dibromide of ethylene, might be expected to be converted into the dibromide of the next higher base; tri-bromethylene thus treated would yield the dibromide of tetrethylene-diammonium

$[N^2(C^2H^4)]^2Br^2$ , which, subjected to the action of moist oxide of silver, should be

converted into the fixed base  $[N^2(C^2H^4)]^2H^2O^2$ . These reactions do, in some measure, actually occur, but they assume a much more complicated character, in consequence of the tendency belonging to dibromide of ethylene of exerting upon the diamines already formed, an action similar to that which it exerted, in the formation of these diamines, upon ammonia itself, thereby giving rise to the formation of triamines, tetramines, and, in general, bases of higher atomicity.

*Ethylene-diamines containing both Monatomic and Diatomic Alcohol-radicles.*—The typic hydrogen of the ethylene-diamines may be replaced by the monatomic alcohol-radicles, methyl, ethyl, &c. Each of these bases, when subjected to the action of *iodide of ethyl*, takes up a quantity of that compound, forming the iodide of a diammonium containing both ethyl and ethylene, and this iodide treated with oxide of silver, yields a diamine in which 2 at. of the original base are replaced by ethyl. Thus, by subjecting monethylene-diamine to the alternate action of iodide of ethyl and oxide of silver, the following series of iodides is obtained:

Di-iodide of Diethyl-ethylene-diammonium . . .  $[N^2H^4(C^2H^5)(C^2H^4)]I^2$ .

Di-iodide of Tetrethyl-ethylene-diammonium . . .  $[N^2H^4(C^2H^5)(C^2H^4)]I^2$ .

Di-iodide of Pentethyl-ethylene-diammonium . . .  $[N^2H^4(C^2H^5)(C^2H^4)]I^2$ .

Di-iodide of Hexethyl-ethylene-diammonium . . .  $[N^2(C^2H^5)(C^2H^4)]I^2$ .

The first two iodides treated with oxide of silver yield volatile bases; the third and fourth yield the fixed bases  $N^2H(C^2H^5)(C^2H^4)H^2O^2$ , and  $N^2(C^2H^5)(C^2H^4)H^2O^2$ , bearing a close resemblance to hydrate of tetrethylammonium, the base with 6 at. of ethyl being incapable of taking up any more ethyl.

Diethylene-diamine subjected to the same alternate treatment with iodide of ethyl and oxide of silver, yields only three bases, one volatile and two fixed. The corresponding iodides are:

Di-iodide of Diethyl-diethylene-diammonium . . .  $[N^2H^4(C^2H^5)(C^2H^4)]I^2$ .

Di-iodide of Triethyl-diethylene-diammonium . . .  $[N^2H^4(C^2H^5)(C^2H^4)]I^2$ .

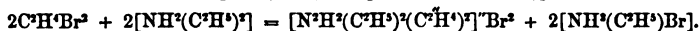
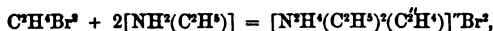
Di-iodide of Tetrethyl-diethylene-diammonium . . .  $[N^2(C^2H^5)(C^2H^4)]I^2$ .

*Iodide of Methyl* acts on the ethylenamines in a similar manner, except that, as in its action on ammonia and the monamines, the final products of substitution are obtained at once, with little or none of the intermediate compounds; thus, with ethylene-diamine, it gives:

Di-iodide of Hexmethyl-ethylene-diammonium,  $[N^2(C^2H^5)(C^2H^4)]I^2$ ,  
and with diethylene-diamine:

Di-iodide of Tetramethyl-diethylene-diammonium,  $[N^2(C^2H^5)(C^2H^4)]I^2$ .

The dibromides of diethyl-ethylene-diammonium and diethyl-diethylene-diammonium are obtained, together with other products, by the action of dibromide of ethylene on ethylamine:

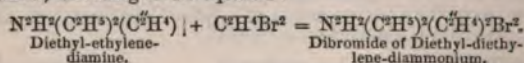


The former of these bromides yields, by distillation with anhydrous baryta, a liquid, which has a strong ammoniacal odour, and solidifies to a crystalline mass, somewhat like fused stearic acid. It may be regarded as

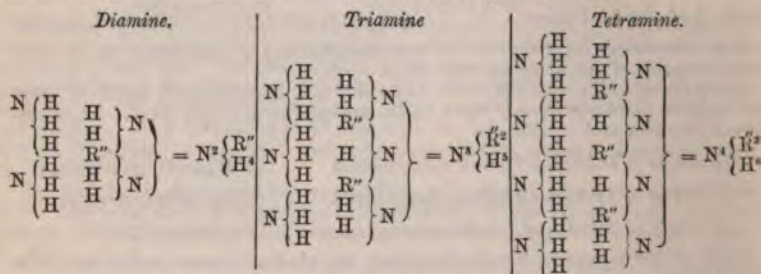
Oxide of Diethyl-ethylene-diammonium . . .  $[N^2H^4(C^2H^3)^2(C^2H^4)]^2O$  ;  
 or, Hydrate of Diethyl-ethylene-diamine . . .  $[N^2H^2(C^2H^3)^2(C^2H^4)] \cdot H^2O$ .

The anhydrous base  $N^2H^2(C^2H^3)^2(C^2H^4) = C^2H^4N^2$ , is obtained by repeatedly distilling the hydrate with excess of anhydrous baryta. Its vapour-density, determined by experiment, is 57.61 (referred to hydrogen as unity), which agrees very nearly with the number calculated from the formula  $C^2H^4N^2$  for a condensation to 2 vol., viz.  $\frac{6.12 + 16.1 + 2.14}{2} = 58$ . But the hydrated base,  $C^2H^4N^2 \cdot H^2O$ , is found by experiment to have a vapour-density of 33.2, whereas, for a condensation to 2 volumes, it should be  $\frac{116 + 18}{2} = 67$ . This hydrate exhibits, therefore, the same anomaly as the hydrate of ethylene-diamine, that is to say, its vapour, when heated  $15^\circ$  or  $20^\circ$  above its boiling point, splits up into the anhydrous base and water, each of which occupies 2 volumes, and the whole, therefore, 4 volumes. That such is the case may be experimentally demonstrated by confining a quantity of the vapour in a tube standing over mercury, heating it, by means of a glass paraffin-bath, to about  $170^\circ$  C., observing its volume, and then passing up a few pellets of anhydrous baryta: the mercury immediately begins to rise, and the volume of the vapour is soon reduced one-half. (Proc. Roy. Soc. x. 597.)

The second of the above-mentioned bromides, the dibromide of diethyl-diethylene-diammonium, yields, by distillation with baryta, a base, which is liquid at ordinary temperatures, and boils at  $185^\circ$  C. This base is diethyl-diethylene-diamine; it is likewise produced by the action of dibromide of ethylene on diethyl-ethylene-diamine, according to the equation:



**Ethylene-triamines, -tetramines, &c.** The action of dibromide (chloride or iodide) of ethylene on ammonia, gives rise, not only to ethylene-diamines, but likewise to ethylene-bases of higher order, that is to say, bases in which a greater number of ammonia-molecules are joined together by the substitution of ethylene for an equivalent quantity of hydrogen. It is obvious that two molecules of ammonia can be joined together into a stable compound by one molecule of a diatomic radicle, three ammonia-molecules by two molecules of diatomic radicles, four by three, &c., thus:



And generally, to unite  $n$  ammonia-molecules into a stable compound, the number of diatomic radicles which is necessary and sufficient, is  $n-1$ ; but the number of such radicles which enter into the combination, may, of course, be increased by further substitution, so long as there is any hydrogen left to be replaced.

The number of stable compounds which can be formed by the action of  $n$  molecules of dibromide of ethylene, or other diatomic alcohol-radicle on  $2n$  molecules of ammonia, is represented by the following equations:

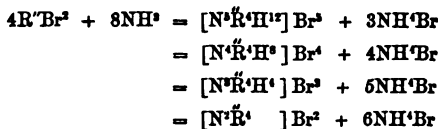
$$\begin{aligned} nR^2Br^2 + 2nNH^3 &= [N^{n+1}R^nH^{2n+4}] Br^{n+1} + (n-1)NH^4Br \\ &= [N^n R^n H^{2n}] Br^n + nNH^4Br \\ &= [N^{n-1}R^n H^{2n-1}] Br^{n-1} + (n+1)NH^4Br \\ &= [N^{n-2}R^n H^{2n-2}] Br^{n-2} + (n+2)NH^4Br \\ &\quad \&c. \&c. ; \end{aligned}$$



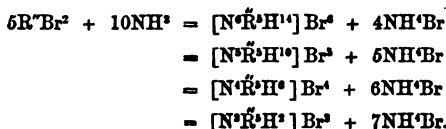
the last term being  $[N^{\frac{n}{2}}\ddot{R}^{\frac{n}{2}}]Br^{\frac{n}{2}} + \frac{3n}{2}NH^{\cdot}Br$ , if  $n$  is even,

or  $[N^{\frac{n+1}{2}}\ddot{R}^{\frac{n+1}{2}}H^{\cdot}]Br^{\frac{n+1}{2}} + \frac{3n-1}{2}NH^{\cdot}Br$ , if  $n$  is odd.

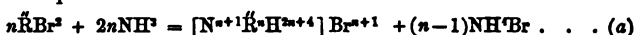
Thus for  $n=4$ , the series of equations representing the possible number of stable polyatomic bases produced is,



and for  $n=5$ ,



The first equation of each series:



represents the formation of the first or simplest term of each polyatomic group, or that in which the replacement of the hydrogen by the diatomic alcohol-radicle is the least that is consistent with stability.

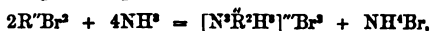
The action of an alcoholic dibromide on primary, secondary, and tertiary monamines, *e. g.* on ethylamine, diethylamine, and triethylamine, is subject to precisely similar laws; but it evidently becomes less complicated, and the number of possible products less numerous, as the number of atoms of replaceable hydrogen in the monamine is diminished.

To return to the general equation just cited. If  $n=1$ , it assumes the simple form:



which, if  $R = C^{\cdot}H^{\cdot}$ , represents the formation of dibromide of ethylene-diammonium, the diamine of which, undergoing further substitution under the influence of dibromide of ethylene, yields the higher terms of the series of diatomic ethylene-bases, *viz.*  $N^2(C^{\cdot}H^{\cdot})^2H^2$  and  $N^2(C^{\cdot}H^{\cdot})^3$ .

When  $n=2$ , the general equation becomes



representing the formation of the first term of a series of tri-ammonium compounds; the following terms of which are  $N^2\ddot{R}^2H^4$ ,  $N^2\ddot{R}^2H^4$ ,  $N^2\ddot{R}^2H^4$  and  $N^2\ddot{R}^2$ .

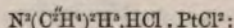
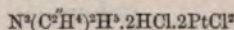
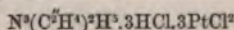
In the ethylene-series, this last equation represents the formation of tribromide of diethylene-triammonium,  $[N^2(C^{\cdot}H^{\cdot})^2H^4]Br^2$ ; which, under the influence of an alkali, yields diethylene-triamine,  $N^2(C^{\cdot}H^{\cdot})^2H^4$ , capable, when subjected to the alternate action of dibromide of ethylene and oxide of silver, or an alkali, of yielding tri-ethylene-triamine,  $N^3(C^{\cdot}H^{\cdot})^3H^6$ , and other triamines of higher degrees of substitution.

The portion of the mixture of volatile bases, obtained by the action of ammonia on dibromide of ethylene, which, after several rectifications, boils between  $200^{\circ}$  and  $220^{\circ}$  C., consists almost wholly of di- and tri-ethylene-triamine. These bases cannot be separated by distillation, in consequence of the proximity of their boiling points; but their separation is effected by transforming them into platinum-salts, which crystallise with remarkable facility.

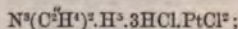
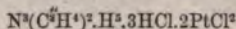
Both diethylene-triamine and triethylene-triamine are powerfully alkaline liquids; soluble in every proportion in water and alcohol, almost insoluble in ether. They boil respectively at about  $208^{\circ}$  and  $216^{\circ}$  C. They neutralise acids completely, giving rise to the formation of well-defined and in most cases beautifully crystallised salts, which are generally very soluble in water, sparingly soluble in alcohol, insoluble in ether. The aqueous solutions of the salts are not precipitated by solutions of caustic alkalis, but solid hydrate of potassium separates their bases in the form of nearly colourless oily liquids, which rapidly attract carbonic acid from the air.

Both these bases, and indeed the triamines generally, are capable of forming three classes of salts, containing respectively 3, 2 and 1 molecule of acid; thus, diethylene-

triamine appears to form three *hydrochlorates*, containing  $N^3(C^2H^4)^2H^3.3HCl$ ,  $N^3(C^2H^4)^2H^2.2HCl$ , and  $N^3(C^2H^4)^2H^1.HCl$ , the latter being still doubtful, but the two former being established by numerous experiments. The *platinum-salts* appear to exhibit a still greater diversity of composition, being capable, not only of forming salts corresponding to the three hydrochlorates just mentioned; viz.



but likewise compounds in which the number of dichloride-of-platinum molecules diminishes, whilst the amount of hydrochloric acid remains constant; such as



not to speak of water of crystallisation, which many of these salts retain with great pertinacity.

This great diversity of salts introduces considerable difficulty into the process of separating the two bases by converting them into saline compounds; most of the salts, however, and especially the platinum-salts, crystallise very readily, a circumstance which greatly facilitates the determination of the conditions under which the more important salts are produced.

The triplatinic salt of diethylene-triamine,  $C^4H^{12}N^3.3HCl.3PtCl^2$ , crystallises in magnificent golden-yellow needles. It cannot be recrystallised without decomposition; a peculiarity which likewise belongs to the platinum-salts of several other triatomic ammonias. New platinum compounds are thus produced, in some of which the chloride is united with a smaller number of molecules of platonic chloride; whilst others, almost insoluble in water, and containing a very large amount of platinum, appear to be produced by platonic substitution.

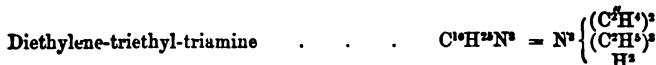
Triethylene-triamine,  $C^6H^{18}N^3 = N^3(C^2H^4)^3H^3$ , forms salts of greater solubility than those of diethylene-triamine, and exhibits a greater tendency to form imperfectly saturated salts; indeed, the normal or triacid salts of this base are obtained only in presence of a large excess of acid, feebly acid solutions always depositing salts containing 2 at. acid to 1 at. of the base; and these diacid salts, when mixed with the free base, yield salts approaching in composition to the mono-acid salts, *e.g.*  $C^6H^{18}N^3.HBr$ , though these last have not been obtained quite pure.

The *normal platinum-salt*,  $C^6H^{18}N^3.3HCl.3PtCl^2$ , crystallises in long gold-coloured needles, much more soluble in water than the platinum-salts of the ethylene-diamines as well as of diethylene-triamine, with which the triethylene-triamine is likely to be contaminated. It cannot be recrystallised without suffering decomposition like the diethylenic platinum-salt above mentioned. Left in contact with an excess of the triacid hydrochlorate of triethylene-triamine, it changes, after a day or two, into well-formed prisms of considerable size, containing about 8 per cent. of platinum less than the original salt, and apparently consisting of a platinum-compound the constitution of which is not yet perfectly established.

The *normal gold-salt*  $C^6H^{18}N^3.3HCl.3AuCl^3$  crystallises in yellow plates soluble in water, alcohol, and ether: they may be recrystallised from water, but on protracted ebullition they are decomposed, with separation of metallic gold.

*Ethylated Triamines.*—The ethylene-triamines just described are powerfully acted on by the iodides of methyl and ethyl, doubtless producing ethylated or methylated ethylene-triamines. The products thus formed have not however been examined in detail, but some of the ethylated derivatives of the ethylene-triamines have been obtained by the action of dibromide of ethylene on ethylamine. This reaction, as already observed (p. 587), yields a mixture of bases, which may be partly separated by fractional distillation. The portion which, after several rectifications, passes over below  $200^\circ$  C. consists mainly of two ethylated diamines,  $N^2(C^2H^4)(C^2H^3)H^2$ , and  $N^2(C^2H^4)^2(C^2H^3)^2$ .

The portion of the mixture boiling above  $200^\circ$  contains the ethylated triamines. Dissolved in hydrochloric acid and mixed with dichloride of platinum, it yields a splendidly crystallised platinum-salt, which, by numerous crystallisations, may be separated into two salts, one sparingly soluble, the other more soluble in water. They consist of the platinum-salts of the two bases:

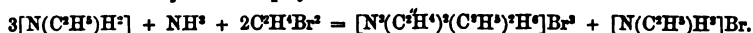


Both these bases are oily liquids, powerfully caustic, extremely soluble in water, boiling between  $220^\circ$  and  $250^\circ$  C. Both form neutral crystalline salts very soluble in water, likewise, though less so, in alcohol. The gold and platinum salts of diethylene-triethyl-triamine, which have the normal composition, crystallise well.

The salts of the second bases are even more soluble than those of the first: the platinum-salt crystallises only when the solution is evaporated nearly to dryness.

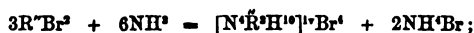


found among the bases of higher boiling-point produced by the action of dibromide of ethylene on ethylamine. Its formation is due to the presence of small quantities of ammonia in the ethylamine employed:



This base forms remarkably beautiful crystalline salts, among which the *hydrochlorate*,  $\text{C}^8\text{H}^{10}\text{N}^3.3\text{HCl}$ , is distinguished by its insolubility in alcohol, a property which renders it easy to separate this base from the other bases accompanying it. The *hydrochlorate* crystallises in leaves having a nacreous lustre: it is very soluble in water, insoluble in ether. The corresponding *hydriodate*,  $\text{C}^8\text{H}^{10}\text{N}^3.3\text{HI}$ , is much more soluble, and is formed only when a great excess of acid is present. In fact, the ethylated ethylene-triamines exhibit the same tendency to form diatomic salts as the ethylene-triamines themselves. A solution of diethylene-diethyl-triamine just neutralised with hydriodic acid, deposits the salt  $\text{C}^8\text{H}^{10}\text{N}^3.2\text{HI}$ . The *nitrate*,  $\text{C}^8\text{H}^{10}\text{N}^3.3\text{HNO}^3$ , dissolves readily in hot, moderately in cold water, and is deposited from a hot saturated solution on cooling in large rectangular tables having the aspect of nitrate of silver.

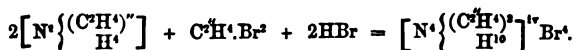
**TETRAMINES.**—The general equation  $a$  (p. 589), when  $n = 3$ , becomes:



showing that the simplest tetramine of the ethylene series is:



The separation of this base among the products of the action of dibromide of ethylene on ammonia is attended with very great difficulty, on account of its high boiling point; but it may be obtained pure by submitting ethylene-diamine to the action of dibromide of ethylene:

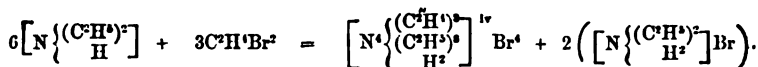
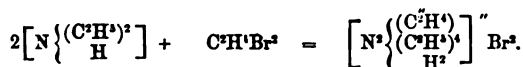


The hydrobromic acid which appears in this equation arises from another phase of the reaction not yet completely studied.

Triethylene-tetramine, separated from the bromide by oxide of silver, is a powerfully alkaline liquid, which dries up to a syrup, showing no tendency to crystallise. The platinum-salt,  $\text{C}^6\text{H}^{10}\text{N}^4.4\text{HCl}.4\text{PtCl}^2$ , is pale yellow, amorphous, almost insoluble.

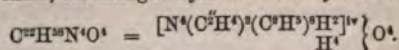
**Ethylated Tetrammoniums.**—These compounds, obtained by the action of dibromide of ethylene on ethylamine and diethylamine, are more easily prepared in a state of purity than the ethylene-tetrammoniums themselves.

Dibromide of ethylene heated with *diethylamine* to  $100^\circ$  C. in sealed tubes for some hours, forms three bromides, viz. bromide of diethylammonium, dibromide of ethylene-tetrethyl-diammonium, and tetrabromide of triethylene-octethyl-tetrammonium:



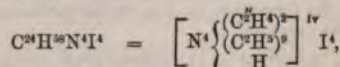


On treating this mixture of bromides with oxide of silver, and subjecting the liberated bases to a protracted current of steam, diethylamine and ethylene-tetrethyl-diamine,  $N^2C^2H^4(C^2H^3)^4$ , which are volatile, pass off with the steam, while a fixed alkaline base remains behind, consisting of hydrate of triethylene-octethyl-tetrammonium:



This base forms well defined salts. The *platinum salt*, almost insoluble in water, separates from a dilute and gently warmed solution in small crystalline plates containing  $C^{12}H^{16}N^4Cl^4.4PtCl^2$ . This salt treated with sulphuretted hydrogen is converted into the soluble chloride, which yields with trichloride of gold a crystalline *gold-salt* containing  $C^{12}H^{16}N^4Cl^4.4AuCl^3$ . The *iodide*,  $C^{12}H^{16}N^4I^4$ , is obtained by treating the free base with hydriodic acid. It is very soluble in water, but may be obtained in white crystals by solution in alcohol and evaporation.

The octethylated base treated with iodide of ethyl, yields the iodide of triethylene-nonethyl-tetrammonium:

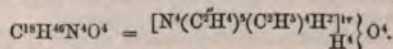


which forms very fine crystals less soluble in alcohol than the octethylated iodide.

When dibromide of ethylene is heated with *ethylamine* to  $100^\circ C.$ , in sealed tubes, a more complicated reaction takes place, giving rise to the formation of six, and occasionally of seven bromides, viz.:

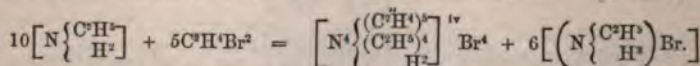
Bromide of Ethylammonium . . . . .	$[N\left\{\frac{C^2H^4}{H^2}\right\}Br]$
Dibromide of Ethylene-diethyl-diammonium . . . . .	$[N^2\left\{\frac{(C^2H^4)^2}{(C^2H^3)^2H^2}\right\}Br^2]$
Dibromide of Diethylene-diethyl-diammonium . . . . .	$[N^2\left\{\frac{(C^2H^4)^2}{(C^2H^3)^2H^2}\right\}Br^2]$
Tribromide of Diethylene-triethyl-triammonium . . . . .	$[N^3\left\{\frac{(C^2H^4)^3}{(C^2H^3)^3H^2}\right\}Br^3]$
Tribromide of Triethylene-triethyl-triammonium . . . . .	$[N^3\left\{\frac{(C^2H^4)^3}{(C^2H^3)^3H^2}\right\}Br^3]$
Tetrabromide of Pentethylene-tetrethyl-tetrammonium . . . . .	$[N^4\left\{\frac{(C^2H^4)^4}{(C^2H^3)^4H^2}\right\}Br^4]$
Tetrabromide of Hexethylene-tetrethyl-tetrammonium . . . . .	$[N^4\left\{\frac{(C^2H^4)^4}{(C^2H^3)^4H^2}\right\}Br^4]$

The ammonias belonging to the first five of these bromides (which have been already considered) are volatile, and, when separated by oxide of silver, are easily driven off by a current of steam. There then remains a powerfully alkaline liquid, consisting in most cases exclusively of the hydrate of pentethylene-tetrethyl-tetrammonium:



The simple salts of this tetrammonium are extremely soluble and very difficult to crystallise. The *gold-salt*,  $C^{18}H^{26}N^4Cl^4.4AuCl^3$ , and the *platinum-salt*,  $C^{18}H^{26}N^4Cl^4.4PtCl^2$ , on the contrary, are difficultly soluble, and are obtained in an amorphous form, or as very indistinctly crystalline plates.

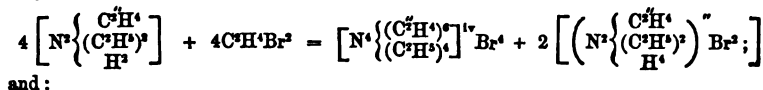
The formation of the pentethylated tetrammonium is represented by the equation,



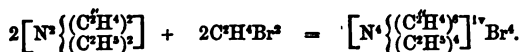
The pentethylated base, which still contains 2 at. of replaceable hydrogen, may with

some difficulty be converted, by the action of iodide of ethyl, first into the pent-ethylene-pentethylated, and lastly into the pentethylene-hexethylated tetrammonium.

Hexethylene-tetrethyl-tetrammonium, which, as already mentioned, is occasionally produced by the action of dibromide of ethylene on ethylamine, may be obtained in a state of purity by the action of dibromide of ethylene on ethylene-diethyl-diamine, or on diethylene-diethyl-diamine; thus:

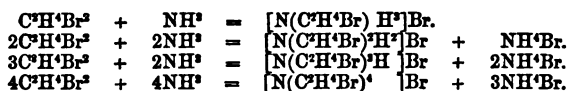


and:



*Monatomic Bases produced by the action of Dibromide of Ethylene on Ammonia and the Monamines.*

The action of ammonia on the bromides of diatomic alcohol-radicles likewise gives rise to the formation of monatomic ammonium-bases, containing monatomic radicles in which 1 atom of hydrogen is replaced by bromine. Thus ammonia and dibromide of ethylene acting upon one another in equal numbers of molecules may produce the following compounds containing the monatomic radicle bromethylammonium,  $C^2H^4Br$ :

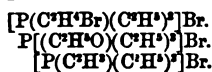


These monatomic bromides differ from the diatomic bromides in this respect, that only half the bromine which they contain is removable by oxide of silver, whereas in the diatomic bromides, both atoms of bromine may be thus removed. (See AMMONIUM-BASES, i. 196.)

Further, if the reaction takes place in presence of water, the bromine within the radicle may be removed in the form of hydrobromic acid, and its place supplied by the molecular residue of the water, HO, producing monatomic bromides containing the radicle oxethyl,  $C^2H^4(HO)$  or  $C^2H^4O$ ; viz.  $[N(C^2H^4O) H^3] Br$ , &c. (the oxethylenamines).

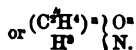
Lastly, a third class of monatomic bromides may be produced in consequence of the tendency of dibromide of ethylene to split up into hydrobromic acid and bromide of vinyl,  $C^2H^3Br$  (p. 569). In this manner the bromides of vinyl-ammonium,  $[N(C^2H^3) H^3] Br$ , and of di-, tri-, and tetra-vinyl-ammonium may be produced.

These reactions are complicated, a very large number of bases being produced at once, so that the separation of them becomes a matter of considerable difficulty. Simpler results are obtained by acting on dibromide of ethylene with ethylamine, diethylamine and triethylamine, the reaction becoming less complicated as the number of atoms of replaceable hydrogen in the amino becomes less; it is especially in the action of dibromide of ethylene on the tertiary amines, that the monatomic bromides are produced: the results suggested by theory for this case are simple, but experiment has failed to produce some of the most interesting terms which are possible. But all the possible compounds are obtained when a tertiary monophosphine is substituted for the tertiary monamine; with triethylphosphine, for instance, the following salts are generated.



(See PHOSPHORUS-BASES.)

**Oxethylenamines or Ethylene-hydoramines.** (A. Wurtz, Compt. rend. xlix. 898; liii. 338; Rép. Chim. pure, 1860, p. 67 and 1861, p. 41.)—Oxide of ethylene unites directly with ammonia in various proportions, forming a series of bases which Wurtz, who discovered them, represents by the general formula  $(C^2H^4O)^n.NH^2$ ,



When oxide of ethylene is placed in contact with a concentrated aqueous solution of ammonia, a powerful action takes place in a few minutes; on evaporating the product over the water-bath, and saturating the syrupy residue with hydrochloric acid, a mixture of the hydrochlorates of three oxethylenic bases is obtained, viz. of mono-, di-, and tri-oxethylenamine, which may be separated by means of absolute alcohol.

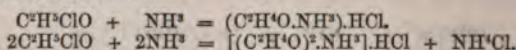
1. The hydrochlorate of trioxethylenamine,  $\left\{ \begin{smallmatrix} \text{C}^2\text{H}^4\text{O} \\ \text{NH}^3 \end{smallmatrix} \right\}^3 \text{HCl}$ , is insoluble in absolute alcohol, and is precipitated on adding that liquid to the mixture.

2. On adding dichloride of platinum to the alcoholic solution, the dioxethylenamine is precipitated in the form of a platinum salt containing  $\left\{ \begin{smallmatrix} \text{C}^2\text{H}^4\text{O} \\ \text{NH}^3 \end{smallmatrix} \right\}^2 \text{HClPtCl}_2$ . If the alcoholic solution contains a little water, as when a strong aqueous solution of chloride of platinum is used, this salt is not entirely precipitated, but the precipitation may then be completed by the addition of ether.

3. If the ether be added in successive small portions, the character of the precipitate gradually changes, and in place of the preceding platinum-salt, which crystallises in splendid rhomboidal prisms, light, golden-yellow, nacreous scales are at length obtained, consisting of the platinum-salt of monoxethylenamine,  $\left\{ \begin{smallmatrix} \text{C}^2\text{H}^4\text{O} \\ \text{NH}^3 \end{smallmatrix} \right\} \text{HClPtCl}_2$ .

The hydrochlorate of monoxethylenamine,  $\left\{ \begin{smallmatrix} \text{C}^2\text{H}^4\text{O} \\ \text{NH}^3 \end{smallmatrix} \right\} \text{HCl}$ , separates spontaneously after a long time from the alcoholic mixture of the hydrochlorates of this and the dioxethylenic base, obtained as above, in small crystals, which may be freed from the thick mother-liquor by rapid washing with absolute alcohol.

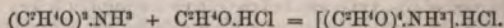
The hydrochlorates of these two bases are likewise formed by heating a mixture of hydroxychloride of ethylene (glycolic chlorhydrin) and aqueous ammonia to  $100^\circ \text{C}$ ., in a strong flask for several hours:



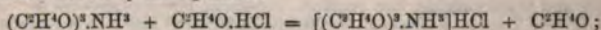
The product of the reaction is evaporated to dryness, and the residue digested with absolute alcohol, which dissolves the two oxethylenic hydrochlorates, and leaves the sal-ammoniac. Hydrochlorate of trioxethylenamine does not appear to be formed in this reaction.

The bases separated from the hydrochlorates by the action of oxide of silver, and evaporated in vacuo, are thick syrupy liquids, having a strong alkaline reaction, and remaining in the form of thick syrups when their solutions are evaporated in vacuo.

*Tetroxethylenamine* or *Tetrethylene-hydoramine*,  $(\text{C}^2\text{H}^4\text{O})^4.\text{NH}^3$ .—When trioxethylenamine is heated in a sealed tube with hydroxychloride of ethylene, a mass of crystals is formed, consisting of the hydrochlorates of tri- and tetra-oxethylenamine, together with a syrupy liquid containing the free tetrethyleneated base. The hydrochlorate of this base is formed by the direct union of the elements of the acting substances:



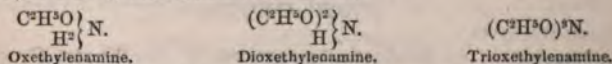
The hydrochlorate of trioxethylenamine is formed, together with oxide of ethylene, in the manner shown by the equation:



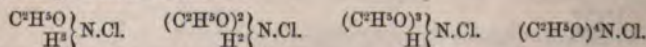
and the oxide of ethylene thus set free unites with another portion of trioxethylenamine, producing the free tetrethyleneated base.

The *chloroplatinate* of this base,  $[(\text{C}^2\text{H}^4\text{O})^4.\text{NH}^3]_4.\text{HClPtCl}_2$ ; crystallises in fine golden-yellow scales, easily soluble in water, insoluble in alcohol and ether.

The mono-, di-, and tri-ethylenated bases, in the free state, may be referred to the type ammonia,  $\text{NH}^3$ , by supposing them to contain the monatomic radicle *oxethylene*,  $\text{C}^2\text{H}^4(\text{HO})$  or  $\text{C}^2\text{H}^4\text{O}$ ; their formulæ then become



Their salts may, of course, be represented as ammonium-salts,—a mode of representation which may also be extended to those of the fourth base; the hydrochlorates, for example, may be formulated thus:



But the fourth base  $(\text{C}^2\text{H}^4\text{O})^4.\text{NH}^3$ , in the anhydrous state cannot be represented as an ammonia. Moreover it is found that trioxethylenamine,  $(\text{C}^2\text{H}^4\text{O})^3.\text{NH}^3$ , can take up, not only 1 at.  $\text{C}^2\text{H}^4\text{O}$  to form the tetrethyleneated base, but likewise 2, 3, 4, &c., molecules of oxide of ethylene, forming bases of greater and greater complexity, and continually diminishing in basic power, but, nevertheless all possessing the same general



characters being capable of turning reddened litmus blue, saturating hydrochloric acid, and forming hydrochlorates which unite with dichloride of platinum. The platinum-salts thus obtained are very difficult to separate one from the other, being non-crystalline gummy masses. Two of them have, however, been obtained in a sufficiently definite state for analysis, and have yielded numbers agreeing approximately with the formulæ  $[(C^2H^4O)^2NH^+].HCl.PtCl_2$  and  $[(C^2H^4O)^2NH^+].HCl.PtCl_4$ . Now, it is impossible to refer these more complex bases, containing more than four molecules of oxide of ethylene, to the ammonium type; hence it is better to regard the whole series of bases as formed on the mixed type,  $\left. \begin{matrix} H^2O \\ H^2N \end{matrix} \right\}$ , or  $\left. \begin{matrix} nH^2O \\ nH^2N \end{matrix} \right\}$ , their general

formula being  $\left. \begin{matrix} (C^2H^4O)^n \\ H^2N \end{matrix} \right\} O^n$  or  $\left. \begin{matrix} (C^2H^4O)^n \\ H^2N \end{matrix} \right\} N^n$ ; hence the name hydoramines, proposed by Kekulé. (See foot-note, vol. i. p. 197.)

This mode of representation may also be extended to those bases produced by the action of dibromide of ethylene on triethylamine and triethylphosphine, which on p. 593 are spoken of as monatomic, and containing the radicles bromethyl and oxethyl, *e. g.*

Bromide of Triethyl-bromethylammonium  $\left. \begin{matrix} (C^2H^5Br)^3 \\ (C^2H^5)^3 \end{matrix} \right\} N.Br = \left. \begin{matrix} (C^2H^5)^3 \\ (C^2H^5)^3 \end{matrix} \right\} Br^3$ .

See the article AMMONIUM-BASES (i. 196); also Kekulé's *Lehrbuch* (p. 558).

For ethylene-bases containing Arsenic, see vol. i. p. 400; for those containing Phosphorus, see PHOSPHORUS-BASES.

A. W. H.

**ETHYLENE-CARBAMIDES.** *Ethylene-ureas.* (Volhard, Proc. Roy. Soc. xi. 268.)—Compounds produced by the action of cyanic acid and the cyanic ethers on the ethylene-diamines.

*Ethylene-dicarbamide.*  $C^2H^4N^2O^2 = N^2(\dot{C}O)^2(C^2H^4)^2H^4$ .—This compound, which contains the elements of 1 at. ethylene-diamine ( $C^2H^4N^2$ ), and 2 at. cyanic acid ( $CHNO$ ), is produced by the action of cyanate of silver on dichloride of ethylene-diammonium. It crystallises in prisms soluble in water and in alcohol; melts at  $192^\circ C$ ; dissolves easily in hydrochloric or nitric acid, and separates out unaltered on evaporation. Boiled with very strong potash-solution, it splits up into ethylene-diamine, carbonic acid, and ammonia:

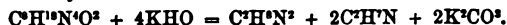


Ethylene-dicarbamide is a *mono-acid tetramine*, forming with dichloride of platinum the salt  $C^2H^4N^2O^2.HCl.PtCl_2$ , and with trichloride of gold, the salt  $C^2H^4N^2.HCl.AuCl_3$ . The platinum-salt crystallises in orange-red prisms; the gold-salt in golden-yellow scales.

*Ethylene-diethyl-dicarbamide.*  $C^2H^4N^2O^2 = N^2(\dot{C}O)^2(C^2H^5)^2(C^2H^5)^2H^4$ .—Of this compound there are two modifications:  $\alpha$  obtained by the action of cyanate of silver on chloride of ethylene-diethyl-diammonium;  $\beta$ , by the direct union of 1 at. ethylene-diamine ( $C^2H^4N^2$ ) with 2 at. cyanate of ethyl ( $C^2H^5NO$ ). Both these bodies crystallise in needles; but  $\alpha$  dissolves very easily in water and in alcohol; melts with partial decomposition at  $124^\circ C$ ., forms a platinum-salt containing  $C^2H^4N^2O^2.HCl.PtCl_2$ , and an unstable gold-salt; whereas  $\beta$ , though easily soluble in boiling water, dissolves with difficulty in cold water, and is even less soluble in alcohol: it melts without decomposition at  $201^\circ C$ ., solidifying again at  $186^\circ$ , and does not unite with the chlorides of gold and platinum. Moreover,  $\alpha$  heated with potash is resolved into ethylene-diethyl-diamine and the products of decomposition of cyanic acid, *viz.* carbonic acid and ammonia:



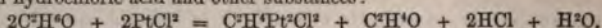
whereas  $\beta$  splits up into ethylene-diamine and the derivatives of cyanic ether, *viz.* carbonic acid and ethylamine:



The two modifications of diethylcarbamide produced, the one by treating cyanate of ethyl with ethylamine or with water (i. 754), the other by the action of cyanic acid on diethylamine, exhibit similar differences, the former splitting up into carbonic acid and ethylamine; the latter into carbonic acid, ammonia, and diethylamine.

**ETHYLENE-DICHLORIDE OF PLATINUM.**  $C^2H^4PtCl_2 = (C^2H^4PtCl_2).Cl$ . *Inflammable or Detonating chloride of platinum, Ethyl-chloroplatinic acid.* (Zeise, [1830] Pogg. Ann. xxi. 497 and 542; xl. 234.—Griess and Martius, Proc. Roy. Soc. xi. 509.—Gm. viii. 388.—Gerh. ii. 316.)—Obtained by distilling alcohol with dichloride of platinum. Aldehyde is then given off, together with hydrochloric acid and chloride of ethyl, and there remains a dark brown liquid, which deposits a large

quantity of a black explosive powder containing ethylene-dichloride of platinum, together with hydrochloric acid and other substances:



*Preparation.*—1. One pt. of dichloride of platinum, as free as possible from protochloride, is dissolved in 10 pts. alcohol of specific gravity 0.823; the solution distilled till the residue is brought down to one-fifth (a very gentle heat only being applied towards the end of the operation, because the mixture is very apt to jump and splash over); the liquid residue filtered to separate it from the black inflammable platinum deposit; the filtrate (the *crude liquid*) cautiously evaporated to dryness; the brown residue, mixed with black and yellow particles, exhausted with cold water; and the yellowish brown solution separated from the undissolved brown gummy substance, and evaporated,—most advantageously in *vacuo*, because in that case there is not so much insoluble brown matter reproduced. The yellow or yellowish brown residue is then redissolved in water, a few brown particles again remaining undissolved, and the filtrate evaporated in *vacuo* over solid potash: ethylene-dichloride of platinum then remains in a state of tolerable purity. (Zeise.)

2. A concentrated aqueous solution of dichloride of platinum is added to a concentrated aqueous solution of the compound of ethylene-dichloride of platinum and sal-ammoniac, as long as a precipitate of chloroplatinate of ammonium continues to fall; the liquid quickly filtered, and evaporated quickly in *vacuo*, first over oil of vitriol, and then over oil of vitriol and hydrate of potash; the gummy and friable residue washed with a small quantity of water to remove any excess of dichloride of platinum, or of the compound of ethylene-dichloride of platinum with sal-ammoniac, that may be present; then dissolved in a larger quantity of lukewarm water, filtered from the chloroplatinate of ammonium, and evaporated in *vacuo*. This method yields the purest product. (Zeise.)

*Properties.*—Ethylene-dichloride of platinum is a very pale lemon-coloured substance, which becomes brown and black by exposure to light, but does not absorb moisture from the air. It dissolves slowly in water and in alcohol. The solutions have an acid reaction, and are very liable to alteration.

*Decompositions.*—1. The compound subjected to dry distillation froths up moderately, gives off a large quantity of hydrochloric acid gas and carburetted hydrogen, and leaves a black residue, which, when heated in the air, burns without flame like charcoal, and leaves metallic platinum.—2. If set on fire in the air before it has been ignited, it burns with flame and leaves metallic platinum having a silvery lustre.—3. The aqueous solution heated to the boiling point quickly becomes turbid, and deposits nearly all the platinum in the metallic state, at the same time giving off hydrochloric acid and a large quantity of combustible gas, but neither alcohol nor ether. the solution likewise becomes decolorised and deposits a brown mucus, even at ordinary or slightly elevated temperatures, especially if exposed to light. The aqueous solution of the pure compound obtained by the second mode of preparation may be evaporated in *vacuo* without decomposition; but the solution of the compound prepared by the first method suffers some degree of decomposition when thus evaporated. If, however, a large quantity of hydrochloric acid be added to the aqueous solution, it is not decomposed even by boiling.—4. If *nitrate of silver* be added to the aqueous solution just so long as a precipitate of chloride of silver continues to form—and the liquid be then filtered, the filtrate becomes turbid in a few minutes and soon yields a large quantity of black pulverulent platinum-deposit, which increases considerably on the application of heat; after which the filtrate will again throw down chloride of silver from a solution of the nitrate. Part of the chlorine is therefore more intimately combined than the rest.—5. The aqueous solution, mixed with excess of *potash*, yields, after a few days, a brown-grey gummy deposit, retaining, however, a considerable quantity of platinum, which is not precipitated till the liquid is heated. If the aqueous solution be immediately heated with excess of potash, it gives off a gas and a distillate which smells like tallow, and deposits a black powder mixed with metallic scales, which, when dried and then strongly heated, detonates with violence; it also sets fire to alcohol.—6. The aqueous solution acts with *magnesia* in the same manner as with cold potash, forming a powder, which when freed from magnesia by dilute nitric acid, and well washed and dried in *vacuo*, likewise explodes violently when heated.—7. *Copper and mercury* throw down from the aqueous solution a black precipitate which detonates when heated.—8. *Sulphydric acid gas* passed through the aqueous solution eliminates a gas, decolorises the liquid completely, and forms a yellow precipitate, which soon turns black. The filtered liquid contains nothing but hydrochloric acid. (Zeise.)

*Combinations.*—Ethylene-dichloride of platinum unites with ammonia, with the chlorides of ammonium, potassium, and sodium, and with the chlorides of several organic bases.

*Ethylene-ammonio-dichloride of Platinum.*  $\text{NH}^3.\text{C}^2\text{H}^4\text{Pt}^2\text{Cl}_2 = [\text{C}^2\text{H}^4(\text{NH}^3)$



$\text{Pt}^2\text{Cl}_2\cdot\text{Cl}$ .—Obtained by precipitating a concentrated aqueous solution of ethylene-dichloride of platinum, or its compound with sal-ammoniac or chloride of potassium, with a slight excess of caustic ammonia or carbonate of ammonia. If the compound with chloride of potassium be used, that salt is found in the filtrate. With the sal-ammoniac compound, potash may be used for the preparation instead of ammonia. Caustic ammonia in large excess exerts a decomposing action on the compound: hence it is better to use carbonate of ammonia. (Zeise.)

The bulky, and at first light-yellow precipitate blackens by exposure to air and light; its colour is also gradually changed by the action of water or alcohol. When subjected to dry distillation, it gives off a combustible gas, hydrochloric acid gas, and sal-ammoniac, and leaves a mixture of platinum and charcoal. As it burns in the air, the mass finally takes fire from end to end. The compound dissolves in water somewhat more readily than gypsum; the solution treated with potash gives off ammonia, and when heated with an acid deposits metallic platinum. Alcohol appears to dissolve the compound more readily than water. Dilute hydrochloric acid colours it a darker yellow, and then dissolves it, producing the following compound. (Zeise.)

*Ethylene-dichloride of Platinum with Sal-ammoniac. Inflammable Chloroplatinate of ammonium.*—The crude liquid (p. 596), which should not be rendered turbid by a concentrated solution of chloride of potassium, is diluted with a four-fold quantity of water, and decanted from the detonating platinum-deposit; a quantity of sal-ammoniac, amounting to 18 per cent. of the dichloride of platinum used to form the crude liquid is then dissolved in it; the solution evaporated down to one-third; the brown crystalline mass which forms on cooling broken up, and dissolved in a small quantity of warm water, after the very acid mother-liquid has run off; the solution evaporated at a gentle heat and cooled to the crystallising point; the crystals washed with a small quantity of water, then dissolved in a larger quantity; and the solution is left to crystallise by evaporation in vacuo.

Lemon-yellow, transparent, shining, oblique rhombic prisms, often half an inch long, which become covered with a black film on exposure to air and light. (Zeise.)

The crystals contain 6.18 per cent. ( $1\frac{1}{2}$ , or perhaps more correctly 1 at.) water of crystallisation, which they give off at  $100^\circ\text{C}$ . or in vacuo, without further decomposition; heated to redness in the air, they leave platinum. Their aqueous solution, when heated alone, or mixed either hot or cold with excess of potash, exhibits the same decompositions as the solution of ethylene-dichloride of platinum heated alone. Mixed with caustic potash and evaporated, it yields a white precipitate. The crystals dissolve in less than 5 pts. of cold water, more sparingly in alcohol. (Zeise.)

*Ethylene-dichloride of Platinum with Chloride of Potassium.  $\text{C}^2\text{H}^4\text{Pt}^2\text{Cl}_2\cdot\text{KCl}$ . Inflammable Platinopotassic Salt.*—Obtained by diluting the crude liquid in the retort (p. 596) with about four times its bulk of water; decanting it from the detonating platinum-deposit; dissolving in it a quantity of chloride of potassium equal to  $\frac{1}{2}$  of the dichloride of platinum used for the preparation of the crude liquid; and otherwise proceeding as in the preparation of the sal-ammoniac compound.

Large lemon-yellow, transparent, shining, oblique rhombic prisms.  $\alpha\text{P} : \infty\text{P} = 103^\circ 58'$ ;  $\infty\text{P} : \infty\text{P} = 112^\circ 5'$ . (Forchhammer.) Reddens litmus. Has a persistently astringent and metallic taste. Dissolves in 5 pts. warm water, less easily in alcohol.

The crystallised salt exposed to light and air becomes covered with a black crust. It contains 4.72 per cent. (1 at.) water of crystallisation, which it gives off completely between  $100^\circ$  and  $150^\circ\text{C}$ . in a current of dry air; it likewise effloresces at ordinary temperatures in very dry air, and quickly in vacuo. The dry salt blackens at about  $200^\circ$ ; gives off without any tumefaction a mixture of 2 vols. hydrochloric acid gas and 1 vol. combustible gas; and leaves a grey mass containing chloroplatinate of potassium (Zeise). According to Griess and Martius, the gas evolved consists of ethylene, the decomposition taking place as shown by the equation:  $\text{C}^2\text{H}^4\text{Pt}^2\text{Cl}_2\cdot\text{KCl} = \text{Pt}^2\text{Cl}_2 + \text{KCl} + \text{C}^2\text{H}^4$ .

Chlorine gas acts on the dry salt only when aided by heat; it then forms hydrochloric acid and trichloride of carbon. Chlorine, bromine, and iodine, added to the aqueous solution of the salt, emit an odour of ether. The dry pulverised salt heated in a stream of hydrogen gas, blackens and exhibits traces of moisture, but does not undergo complete decomposition till it is heated in the current of gas. A stream of hydrogen passed through the aqueous solution throws down metallic platinum. The aqueous solution exhibits, with nitrate of silver, the same reaction as ethylene-dichloride of platinum alone. At  $90^\circ\text{C}$ . it decomposes rapidly, but a certain quantity of platinum always remains in solution. In this case also hydrochloric acid, as well as sulphuric and nitric acid, prevents the decomposition, even at the boiling heat; an excess of chloride of potassium appears also to exert a protecting action.



*Ethylene-dichloride of Platinum with Chloride of Sodium.*—Difficult to crystallise; dissolves somewhat slowly in alcohol, forming a yellow solution, unless an acid is present.

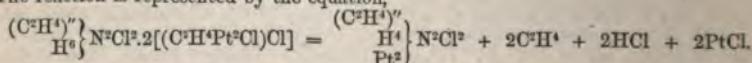
*Compounds of Ethylene-dichloride of Platinum with the Chlorides of Organic bases.*—A number of these compounds have been obtained by Griess and Martius, but no detailed description of them has yet been published. These compounds, most of which form very fine crystals, may be arranged in two series, comparable in many respects with certain classes of compounds which protochloride of platinum forms with organic bases. Regarding ethylene-dichloride of platinum as the chloride of a monatomic radicle,  $C^2H^4Pt^2Cl$ , a very simple relation between the compounds of this body and those of protochloride of platinum becomes perceptible; thus—

Compounds of Protochloride of Platinum.		Compounds of Ethylene-dichloride of Platinum.	
<i>First Series.</i>			
PtCl	. . . . .	$(C^2H^4Pt^2Cl).Cl$	
$H^1NCl.PtCl$	. . . . .	$H^1NCl.(C^2H^4Pt^2Cl).Cl$	
$C^2H^3 \left\{ \begin{array}{l} H^1 \\ H^2 \end{array} \right\} NCl.PtCl$	. . . . .	$C^2H^3 \left\{ \begin{array}{l} H^1 \\ H^2 \end{array} \right\} NCl.(C^2H^4Pt^2Cl).Cl$	
$(C^2H^4)'' \left\{ \begin{array}{l} H^1 \\ H^2 \end{array} \right\} N^2Cl^2.2PtCl$	. . . . .	$(C^2H^4)'' \left\{ \begin{array}{l} H^1 \\ H^2 \end{array} \right\} N^2Cl^2.2[(C^2H^4Pt^2Cl).Cl]$	
<i>Second Series.</i>			
$H^3 \left\{ \begin{array}{l} Pt \\ Pt \end{array} \right\} NCl$	. . . . .	$C^2H^3 \left\{ \begin{array}{l} H^3 \\ Pt^2 \end{array} \right\} NCl$	
$C^2H^3 \left\{ \begin{array}{l} H^1 \\ Pt \end{array} \right\} NCl$	. . . . .	$C^2H^3 \left\{ \begin{array}{l} H^2 \\ Pt^2 \end{array} \right\} NCl$	
$(C^2H^3)^2 \left\{ \begin{array}{l} H \\ Pt \end{array} \right\} NCl$	. . . . .	$(C^2H^3)^2 \left\{ \begin{array}{l} H \\ Pt^2 \end{array} \right\} NCl$	
$(C^2H^4)'' \left\{ \begin{array}{l} H^1 \\ Pt^2 \end{array} \right\} N^2Cl^2$	. . . . .	$(C^2H^4)'' \left\{ \begin{array}{l} H^1 \\ Pt^2 \end{array} \right\} N^2Cl^2$	
		$(C^2H^4Pt^2Cl)^2$	

When the aqueous solution of the last compound in the first of the above series, viz.  $(C^2H^4)'' \left\{ \begin{array}{l} H^1 \\ H^2 \end{array} \right\} N^2Cl^2.2[(C^2H^4Pt^2Cl).Cl]$ , is boiled, a considerable quantity of gas is evolved;

and beautiful yellow sparingly soluble needles are deposited, containing  $(C^2H^4)'' \left\{ \begin{array}{l} H^1 \\ Pt^2 \end{array} \right\} N^2Cl^2$ .

The reaction is represented by the equation,



**ETHYLENE-HYDORAMINES.** See ETHYLENE-BASES (p. 594).

**ETHYLENE-PHENYLAMINES.** See PHENYLAMINE.

**ETHYLENE-PHOSPHINES.** See PHOSPHORUS-BASES.

**ETHYLENE-SUCCINIC ACID.** See ETHYLENE, SUCCINATE OF (p. 582).

**ETHYLENE-SULPHURIC ACID.** See ETHYLENE, SULPHATE OF (p. 582).

**ETHYLENE-SULPHUROUS ACIDS.** See SULPHUROUS ETHERS.

**ETHYLENE-TETRAMINES and TRIAMINES.** See ETHYLENE-BASES.

**ETHYLENE-UREAS.** See ETHYLENE-CARBAMIDES (p. 595).

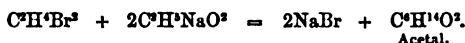
**ETHYLIDENE.**  $C^2H^4$ .—A radicle not known in the separate state, but supposed to exist in certain compounds derived from aldehyde and isomeric with the corresponding compounds of ethylene; e.g.:

Ethylidene-compounds.		Isomeric with	
Aldehyde	$C^2H^4O$	Oxide of Ethylene	$C^2H^4O$
Chloride of Ethylidene	$C^2H^4Cl^2$	Chloride of Ethylene	$C^2H^4Cl^2$
Compound of Aldehyde and Acetic Anhydride	$C^2H^4O.C^2H^3O^2$	Diacetate of Ethylene	$C^2H^4.(C^2H^3O^2)^2$
Compound of Aldehyde and Chloride of Acetyl	$C^2H^4O.C^2H^3OCl$	Acetoxychloride of Ethylene	$C^2H^4.C^2H^3O^2.Cl$
Acetal	$C^2H^4O^2$	Diethylate of Ethylene	$C^2H^4.(C^2H^3O)^2$

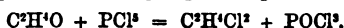
These two series of compounds are intimately related to each other, and *chloride of vinyl*,  $C^2H^3Cl$ , which may be produced from either of them, may be regarded as the link between the two.

**Bromide of Ethylidene.**  $C^2H^3Br^2$ . (Wurtz and Frapolli, Ann. Ch. Pharm. cviii. 225.)—This compound is obtained by passing vapour of aldehyde over pentabromide of phosphorus in a vessel externally cooled. The products are bromide of ethylidene and oxybromide of phosphorus ( $C^2H^3O + PBr^3 = C^2H^3Br^2 + PBr^2O$ ), which cannot be separated by fractional distillation, because the bromide of ethylidene is decomposed by heat. The oxybromide of phosphorus may, however, be removed by agitating the mixture with lumps of ice, replacing them as they melt. A dense yellow liquid is thus obtained, which is insoluble in water and is readily decomposed by water, with evolution of hydrobromic acid: hence it is impossible to obtain the compound in a state of sufficient purity for analysis.

Bromide of ethylidene treated with ethylate of sodium yields acetal:



**Chloride of Ethylidene.**  $C^2H^3Cl^2$ . (Geuther, Ann. Ch. Pharm. cv. 321.—Wurtz and Frapolli, Compt. rend. xlvii. 418; Ann. Ch. Pharm. cviii. 223.)—Produced by the action of pentachloride of phosphorus upon aldehyde:



Glycol treated with pentachloride of phosphorus yields the isomeric compound, chloride of ethylene.

The vessel containing the chloride of phosphorus must be kept cool, while the aldehyde is added by small portions; afterwards the mixture is warmed, whereupon the whole dissolves to a homogeneous liquid, which gradually blackens when distilled, and gives off below  $100^\circ C$ . a liquid, from which water separates an oily body, and above  $100^\circ$  oxychloride of phosphorus. The oily liquid, dried by chloride of calcium and rectified, yields chloride of ethylidene.

Chloride of ethylidene is a transparent, colourless, oily liquid, resembling chloroform in taste and odour. Specific gravity 1.189 at  $4.3^\circ C$ . (Geuther). Boils at  $68^\circ$  (Wurtz and Frapolli), at  $60^\circ$  (Geuther).

It is isomeric with chloride of ethylene, but differs from it in specific gravity and in boiling point, the specific gravity of chloride of ethylene being 1.256 at  $12^\circ C$ . according to Regnault, and the boiling point  $86^\circ$  according to Dumas. The two bodies differ also in their behaviour with alcoholic potash, chloride of ethylene being easily decomposed thereby into chloride of potassium and the compound  $C^2H^3Cl$ ; whereas chloride of ethylidene is not at all affected by alcoholic potash in the cold, and with difficulty even when heated. It appears also to be identical with monochlorinated chloride of ethyl,  $C^2H^3Cl.Cl$  (p. 531), that compound having a specific gravity of 1.174 at  $17^\circ C$ ., and boiling at  $64^\circ$ . (Beilstein, Bull. Soc. Chim. de Paris, i. 60.)

Chloride of ethylidene, treated with ethylate of sodium, does not act like the bromide and produce acetal, but yields a gas identical in composition and properties with chloride of vinyl ( $C^2H^3Cl$ ).

**Oxychloride of Ethylidene.**  $C^2H^3Cl^2O = (C^2H^3)^2 \left\{ \begin{smallmatrix} Cl^2 \\ O \end{smallmatrix} \right.$  (A. Lieben, Compt. rend. xlii. 662; Ann. Ch. Pharm. cvi. 336.)—This compound, which is isomeric with monochlorethyl ether (p. 540), and may be regarded as a double molecule of aldehyde, in which 1 at. O is replaced by 2 at. Cl, is produced by the action of hydrochloric acid on aldehyde:



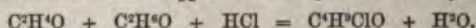
When aldehyde cooled by a freezing mixture is saturated with dry hydrochloric acid gas, the liquid increases in volume and separates into two colourless layers, which must be immediately separated, as they act upon each other. The lower layer is aqueous hydrochloric acid; the upper is oxychloride of ethylidene, which may be purified by repeated distillation over chloride of calcium.

Transparent, colourless liquid, smelling of aldehyde and hydrochloric acid. Specific gravity 1.1376 at  $12^\circ C$ . Boiling point  $116^\circ$ — $117^\circ$ . Vapour-density 5.08 (taken at  $173^\circ$ ); calc. (2 vol.) = 4.95.

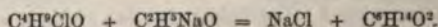
Oxychloride of ethylidene is not decomposed by water in the cold, but on heating it is converted thereby into hydrochloric acid and aldehyde. Pentachloride of phosphorus does not act upon it at ordinary temperatures, but when heated with it in a sealed tube to  $100^\circ C$ . for several hours, it dissolves completely: the organic product cannot, however, be separated from the oxychloride of phosphorus formed at the same time. (Wurtz and Frapolli.)

Geuther and Cartmell, by treating aldehyde with hydrochloric acid, have obtained, besides the oxychloride just described, another which has the composition  $C^2H^3ClO^2$ , and may be regarded as a triple molecule of aldehyde,  $C^2H^{12}O^3$ , in which 1 at. O is replaced by 2 at. Cl. (Proc. Roy. Soc. x. 110.)

**Chlorethylate of Ethylidene.**  $C^2H^3ClO = C^2H^4.C^2H^3O.Cl$ . (Wurtz and Frapolli, Ann. Ch. Pharm. cviii. 226.)—Produced by passing hydrochloric acid to saturation into a mixture of 1 vol. aldehyde and 2 vol. absolute alcohol, surrounded with a freezing mixture. Two layers of liquid are then formed, the lower consisting of aqueous hydrochloric acid and the upper ethereal layer of chlorethylate of ethylidene:



This compound, treated with ethylate of sodium, yields chloride of sodium and acetal:



**ETHYL-FORMAMIDE.** See FORMAMIDE.

**ETHYL-FORMYL.** Löwig's name for PROPYLENE or TRITYLENE. ( $C^2H^3 = C^2H^3.CH$ .)

**ETHYL-HEMIPINIC ACID.** See HEMIPINIC ETHERS.

**ETHYLIA.** Syn. with ETHYLAMINE.

**ETHYLIDES** or **ETHIDES.** Compounds of ethyl with elementary bodies or with other alcohol-radicles.

**ETHYL-LACTIC ACID.** See LACTIC ETHERS.

**ETHYL-MALIC ACID.** See MALIC ETHERS.

**ETHYL-MECONIC ACID.** See MECONIC ETHERS.

**ETHYL-MELLIC ACID.** See MELLIC ETHERS.

**ETHYL-MERCAPTAN.** Syn. with ETHYL, SULPHYDRATE OF (p. 547).

**ETHYL-METHYLAMINES.** See METHYLAMINES.

**ETHYL-METHYL-CONINIUM.** See CONINE (p. 6).

**ETHYL-METHYLIC ETHER.** See ETHYL, OXIDE OF (p. 542).

**ETHYL-MORPHINE.** See MORPHINE.

**ETHYL-MUCIC ACID.** See MUCIC ETHERS.

**ETHYL-NICOTINE.** See NICOTINE.

**ETHYL-NITRANILINE.** See NITRANILINE under PHENYLAMINE.

**ETHYL-NITROPHENIDINE.** See PHENIC ETHERS.

**ETHYL-OCTYLIC ETHER.** See ETHYL, OXIDE OF (p. 542).

**ETHYL-OKALIC ACID.** See OKALIC ETHERS.

**ETHYL-OKACETIC ACID.** See OKACETIC ETHER.

**ETHYL-OKAMIC ACID** and **ETHYL-OKAMIDE.** See OKAMIC ETHER and OKAMIDE.

**ETHYL-PARATARTARIC ACID.** See PARATARTARIC ACID.

**ETHYL-PHENYLAMINES.** See PHENYLAMINE.

**ETHYL-PHOSPHINES.** See PHOSPHORUS-BASES.

**ETHYL-PHOSPHORIC** and **-PHOSPHOROUS ACIDS.** See PHOSPHORIC and PHOSPHOROUS ETHERS.

**ETHYL-PICOLINE.** See PICOLINE.

**ETHYL-PIPERIDINE.** See PIPERIDINE.

**ETHYL-PTERITANNIC ACID.** See PTERITANNIC ACID.

**ETHYL-PYRIDINE.** See PYRIDINE.

**ETHYL-QUININE.** See QUININE.

**ETHYL-SELENHYDRIC ACID.** See ETHYL, SELENHYDRATE OF (p. 543).

**ETHYL-SINAMINE.** See SINAMINE.

**ETHYL-STIBINES.** See ANTIMONY-RADICLES, ORGANIC (i. 341).

**ETHYL-STRYCHNINE.** See STRYCHNINE.

**ETHYL-SULPHYDRIC ACID.** See ETHYL, SULPHYDRATE OF (p. 547).



# ETHYL-SULPHOCARBONIC ACID — EUCHROIC ACID. 601

**ETHYL-SULPHOCARBONIC** and **-SULPHOPHOSPHORIC ACIDS.**  
See SULPHOCARBONIC and SULPHOPHOSPHORIC ETHERS.

**ETHYL-SULPHURIC** and **-SULPHUROUS ACIDS.** See SULPHURIC and SULPHUROUS ETHERS.

**ETHYL-TANNASPIDIC ACID.** See TANNIC ACIDS.

**ETHYL-TARTARIC ACID.** See TARTARIC ETHERS.

**ETHYL-THIOSINAMINE.** See THIOSINAMINE.

**ETHYL-TOLUIDINE.** See TOLUIDINE.

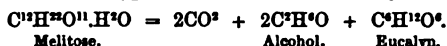
**ETHYL-TRITHIONIC ACID.** See METHYL-DITHIONIC ACID.

**ETHYL-UREA.** See CARBAMIDE (i. 754).

**ETHYL-URETHANE.** See CARBAMIC ACID (i. 751).

**EUCAIRITE.** Syn. with EUKAIRITE.

**EUCALYN.**  $C^6H^{12}O^6$ .—A saccharine substance, produced in the fermentation of melitose (the sugar of the eucalyptus), under the influence of yeast:



It is syrupy, dextro-rotatory ( $[\alpha] = +50^\circ$  nearly), non-fermentable, and does not acquire that property by the action of sulphuric acid. It becomes coloured at  $100^\circ C.$ , and at  $200^\circ$  is converted into a black insoluble substance. Strong sulphuric acid and fuming hydrochloric acid destroy it at  $100^\circ$ . Baryta colours it strongly at the same temperature. It reduces tartrate of copper and potassium. These properties are very similar to those of sorbin.

**EUCALYPTUS.** A genus of Australian plants, one species of which yields, by distillation with water, a volatile oil resembling cajeput oil. Several species of eucalyptus yield the so-called Australian manna, a white, loose, granular mass, in which Johnston found a crystallisable sugar (melitose), containing in the air-dried state, according to his analysis,  $C^{12}H^{22}O^{11}.H^2O$ , and identical with grape-sugar (Mem. Chem. Soc. i. 159). Berthelot (Compt. rend. xli. 392) also finds it to be identical in composition with grape-sugar, and very similar in its reactions; he regards it as a compound of grape-sugar with the isomeric substance eucalyn. (See MELITOSE.)

**EUCAMPTITE.** See EUKAMPTITE.

**EUCHEMA SPINOSUM,** the so-called Agar-agar (i. 61) contains, according to Oudemans (Arch. Pharm. [2] lxxxvii. 283), nothing but the ordinary constituents of plants.

**EUCHELORE.** A gaseous mixture of chlorine and oxide of chlorine, obtained by the action of hydrochloric acid on chlorate of potassium. (See CHLORINE, OXYGEN-COMPOUNDS OF, i. 912.)

**EUCHROIC ACID.**  $C^{12}H^4N^2O^8$ . (Wöhler [1841], Pogg. Ann. lii. 610.—R. Schwarz, Ann. Ch. Pharm. lxxvi. 49).—Regarded by Laurent and Gerhardt as mellamic acid,  $C^6H^2NO^4 = \begin{array}{c} NH^2(C^6O^4) \\ H \end{array} \} O$ .

The ammonium-salt of this acid is obtained, together with paramide, by heating pulverised mellate of ammonium to  $150^\circ$ — $160^\circ$  for several hours, stirring it all the while, and continuing the heating as long as any odour of ammonia is given off. A pale yellow powder then remains, consisting of a mixture of paramide and euchroate of ammonium, the latter of which may be washed out by water, and obtained in crystalline crusts by evaporating the filtered solution. On dissolving this salt in a very small quantity of boiling water, adding hydrochloric or nitric acid to the hot solution, and leaving it to cool, euchroic acid separates in the form of a white crystalline powder, which may be purified by recrystallisation.

Euchroic acid crystallises in very small rhomboïdal prisms, usually grouped in pairs; it is sparingly soluble in cold water, and has a strong acid reaction. At  $200^\circ C.$  it gives off 10.54 per cent., or 2 at. water (Wöhler). The dried acid is found by analysis to contain:

	Dried at $200^\circ C.$		Wöhler.	Schwarz (mean).
$C^{12}$	144	47.37	48.66	47.55
$H^4$	4	1.31	1.66	1.50
$N^2$	28	9.21	10.98	9.18
$O^8$	128	42.11		
	304	100.00		

The analytical numbers agree tolerably well with the formula  $C^{12}H^4N^2O^8$  proposed by Wöhler, according to which euchroic acid is formed from trimellate of ammonium by the abstraction of 4 at. water:



Nevertheless Gerhardt regards the formula  $C^6H^2NO^4$  [ =  $C^6H(NH^4)O^4$  (acid mellamate of ammonium) -  $H^2O$ ] as more in accordance with the mode of formation of the acid, and suggests that, as the acid analysed by Wöhler and by Schwarz was dried at  $200^\circ C$ , it was perhaps partly converted into paramide,  $C^6HNO^3$ , which would increase the proportion of carbon.

The acid remains unaltered at  $280^\circ C$ , but at a higher temperature melts, boils, and decomposes, yielding hydrocyanate of ammonia, and a dark green, bitter sublimate. (Wöhler.)—Zinc, protoxide of iron, or the electric current, throws down from an aqueous solution of euchroic acid a dark blue substance, called euchrone, of unknown composition, insoluble in water, but dissolving with purple colour in alkalis, and quickly oxidising again in the air to euchroic acid (Wöhler).—The deep blue, closely adhering deposit with which zinc becomes covered in the aqueous acid, detaches itself on immersion for a short time in very dilute hydrochloric acid, and may then be collected on a filter, washed, and dried. The black mass thus obtained, which is free from zinc, is instantly oxidised, by the slightest heating, to euchroic acid; it dissolves in aqueous ammonia or potash, with a more splendid colour than that of permanganate of potassium; but the solution becomes decolorised from above downwards, on exposure to the air, and very quickly if agitated. In the boiling acid, zinc acquires a similar coating, but a trace of gas is evolved at the same time, and the liquid deposits a white powder, probably mellate of zinc. A mixture of aqueous euchroic acid and protochloride of iron forms, with alkalis, a thick deep violet-coloured precipitate, which immediately becomes rust-brown on exposure to the air, and dissolves without colour in hydrochloric acid, because the resulting sesquioxide of iron is reduced to the state of protoxide by the euchrone, which is thereby reconverted into euchroic acid. These phenomena are not produced by stannous or manganous chloride. Platinum in galvanic combination with zinc, does not act upon the aqueous acid, but decomposes its ammonia-salt (Wöhler). The aqueous acid is likewise decomposed by the electric current, and covers the negative platinum with a deep blue deposit, which, however, soon ceases to increase. Euchrone is not produced by the action of sulphuretted hydrogen, sulphurous acid, hyposulphites, or arsenites (Schwarz). Euchroic acid mixed with a quantity of water not sufficient to dissolve it in its unaltered state, and heated to  $200^\circ C$ , in a sealed glass tube, dissolves completely in the form of acid mellate of ammonium (Wöhler).



Euchroic acid dissolved in water does not decompose when boiled in contact with the air. Hydrochloric acid and nitric acid exert no decomposing action upon it. (Wöhler.)

Euchroic acid is dibasic, its neutral salts having the composition  $C^{12}(H^4M^2)N^2O^8$ .

*Euchroates of Ammonium.*—The neutral salt,  $C^{12}H^2(NH^4)^2N^2O^8$ , obtained by evaporating the wash-water of paramide, as above described, forms white, scarcely crystalline crusts, which are decomposed by hydrochloric or nitric, but not by acetic acid. (Wöhler.)

An acid salt is sometimes precipitated from the aqueous solution of the neutral salt instead of the pure acid, and separates from solution in hot water, in yellowish crystals larger than those of the pure acid. (Wöhler.)

*Euchroate of Barium*,  $C^{12}H^2Ba^2N^2O^8 + H^2O$ , is precipitated in the form of a pale yellow powder, when baryta-water is dropt into an excess of warm aqueous euchroic acid. (Schwarz.)

An acid barium-salt is obtained, as a pale yellow pulverulent precipitate, on slowly adding baryta-water to a warm solution of euchroic acid in excess. (Schwarz.)

*Euchroate of Lead*,  $C^{12}H^2Pb^2N^2O^8 + H^2O$ .—The boiling aqueous solution of euchroic acid, mixed with a dilute solution of neutral acetate of lead, yields, on cooling, a yellow powder, which appears crystalline under the microscope. (The filtrate separated from this precipitate deposits mellate of lead as a white powder when boiled.) The air-dried salt gives off 11.36 per cent. (3 at.) water at  $160^\circ C$ , but nothing more at a stronger heat till it begins to decompose. (Wöhler.)

*Euchroate of Silver*,  $C^{12}H^2Ag^2N^2O^8$ , is a sulphur-yellow powder, obtained by mixing a boiling aqueous solution of the acid with a dilute solution of nitrate of silver; when treated with ammonia it becomes so gelatinous that it passes through the filters.

**EUCHROITE.** A native arsenate of copper found at Libethen in Hungary. It contains 33.02 per cent. arsenic anhydride, 47.85 cupric oxide, and 18.8 water

(Turner, Ed. Phil. J. iv. 301), whence the formula  $4\text{Cu}^2\text{O} \cdot \text{As}_2\text{O}_3 + 7\text{H}_2\text{O}$ , or  $\text{Cu}^2\text{O} \cdot 2\text{Cu}^2\text{AsO}_4 + 7\text{H}_2\text{O}$ . The crystals belong to the trimetric system. Hardness = 3.5 to 4. Specific gravity 3.35 to 3.45. Colour emerald-green. Streak light apple-green. Lustre vitreous. More or less transparent. (Handw. d. Chem. ii. [3] 943.)

**EUCHRONE.** A product of the decomposition of euchroic acid by zinc and certain other reducing agents (p. 602).

**EUCHYSIDIMITE.** A variety of augite.

**EUCLEASE.** *Prismatic emerald.*—A silicate of aluminium and glucinum, allied to beryl; found in Peru, Brazil, in the Urals, but rare. Crystallises in monoclinic prisms, often modified by numerous faces.  $\infty P : \infty P = 115^\circ 0'$ ;  $\infty P\infty : \infty P = 107^\circ 37' 30''$ . Ratio of principal axis, clinodiagonal and orthodiagonal = 1 : 0.9713 : 3.0008. Cleavage very distinct, parallel to  $\infty P\infty$ ; much less distinct parallel to  $\infty P$  and  $[\infty P\infty]$ . Hardness = 7.5. Specific gravity = 3.0 to 3.1. Colour light yellowish-green to yellow, bluish-green to blue, also white. Lustre vitreous. Transparent to translucent. Fracture conchoidal. Very brittle. When strongly heated before the blowpipe, it swells up and melts in thin splinters to a white enamel. Not attacked by borax or phosphorus-salt. Insoluble in acids.

Euclease was formerly regarded as an anhydrous silicate; but Damour (Compt. rend. xv. 942) has shown that it contains water, his analysis giving:

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Gl}_2\text{O}$	$\text{Ca}^2\text{O}$	$\text{Fe}^2\text{O}$	$\text{SnO}$	$\text{H}_2\text{O}$	F
41.63	34.07	16.97	0.14	1.03	0.34	6.04	0.38 = 100.60

whence the formula  $2\text{Gl}^2\text{O} \cdot \text{SiO}_2 + \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 + \text{aq.}$  or  $\left(\frac{\text{Gl}}{\text{al}}\right)^4 \text{Si}^2\text{O}^6 + 2\text{alHO}$ . (Jahresber. d. Chem. 1852, p. 855; 1853, p. 800; 1855, p. 941.—Dana, ii. 267.—Rammelsberg, p. 671.)

**EUCLASITE.** A name formerly applied to a green apatite from Lake Baikal.

**EUDIALYTE.** A mineral from Kangerdluarsuk in Greenland, crystallised in hemihedral forms of the hexagonal system, the primary form being an acute rhombohedron of  $73^\circ 40'$ , with the faces  $\text{oR}$ ,  $\infty\text{R}_2$ , and other forms subordinate. Cleavage very distinct parallel to  $\text{oR}$ ; less distinct parallel to  $\text{R}$ . Occurs also crystallo-granular, massive, and imbedded. Hardness = 5.0 to 5.5. Specific gravity = 2.9. Colour bluish to brownish-red; streak uncoloured. Lustre vitreous. Opaque to slightly translucent. Before the blowpipe it melts easily to a greyish-green enamel; dissolves with moderate facility in borax, yielding a glass slightly coloured by iron; easily decomposed by phosphorus-salt, with separation of a tumefied skeleton of silica. Easily decomposed by hydrochloric acid, with formation of a jelly.

Eudialyte is essentially a zirco-silicate of sodium and calcium, that is to say, a silicate in which the silicon is partly replaced by zirconium; but it likewise contains tantalum, or rather perhaps niobic acid, and several other constituents.

*Analyses.*—*a.* by Rammelsberg (Pogg. Ann. lxxiii. 142), *b.* by Damour (Compt. rend. xliiii. 1197):

	$\text{SiO}_2$	$\text{ZrO}_2$	$\text{TaO}_2$	$\text{Fe}^2\text{O}$	$\text{Mn}^2\text{O}$	$\text{Ca}^2\text{O}$	$\text{Na}^2\text{O}$	$\text{K}^2\text{O}$	Cl	Loss by ignition
<i>a.</i>	49.92	16.88	.	6.97	1.16	11.11	12.28	0.65	1.19	0.37 = 100.52
<i>b.</i>	50.38	16.60	0.35	6.37	1.61	9.23	13.10	.	1.48	1.25 = 99.37

These analyses lead to the formula  $\text{M}^2\text{O} \cdot 2(\text{SiO}_2; \text{ZrO}_2)$ , or  $\text{M}^2(\text{Si}; \text{Zr})\text{O}_2(\text{Si}; \text{Zr})\text{O}_2$ , analogous to that of a metasilicate with excess of silica. The basic metal M is made up of sodium, calcium, and ferrosium. (Dana, ii. 181.—Rammelsberg, p. 893.)

Closely allied to eudialyte, if not identical with it, is *eukolyte*, from Brevig in Norway (p. 605).

**EUDIOMETER** and **EUDIOMETRY.** See ANALYSIS, VOLUMETRIC, OF GASES (i. 268).

**EUDNOPHITE.** Analcime from the island of Lamö, near Brevig in Norway, supposed by Weibye (Pogg. Ann. lxxix. 303) to differ from ordinary analcime in crystalline form, being trimetric instead of monometric. According to Möller, however (J. pr. Chem. lxxix. 318), this difference does not exist.

**EUGENALLOPHANIC ACID.** See ALLOPHANIC ACID (i. 134).

**EUGENANISIC ANHYDRIDE.**  $\text{C}^{10}\text{H}^{10}\text{O}^4$  = *Eugenanisyl. Aniscugenyl.*—A compound produced by the action of chloride of anisyl on eugenic acid. It is crystallisable and insoluble in aqueous potash. (Cahours, Ann. Ch. Phys. [3] lii. 189.)

**EUGENE-GLANCE.** Syn. with POLYBASITE.



**EUGENESITE.** A name given by Kobell to the palladium from Tilkerode in the Hartz, which crystallises in the hexagonal system and cleaves parallel to the faces of a hexagonal prism.

**EUGENETHYL.** Eugenate of ethyl (*vid. inf.*)

**EUGENIC ACID.**  $C^{10}H^{12}O^2 = \begin{matrix} C^{10}H^{11}O \\ H \end{matrix} \bigg\} O$ . *Eugenol. Caryophyllie acid.*

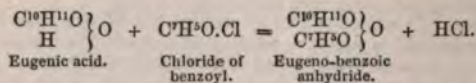
*Oxidised essence of cloves.* (Bonastre [1827], Ann. Ch. Phys. xxxv. 274.—Dumas, *ibid.* liii. 164; also Ann. Ch. Pharm. ix. 65; xxvii. 151.—Ettling, Ann. Ch. Pharm. ix. 68.—Böckmann, *ibid.* xxvii. 155.—C. Gr. Williams, Chem. Gaz. 1858, 170.—Cahours, Ann. Ch. Phys. [3] lii. 201.—Stenhouse, Ann. Ch. Pharm. xev. 103.—Baeyer, Ann. Ch. Pharm. cxiv. 163.—Gm. xiv. 201.)—When cloves are distilled with water, a distillate (crude oil of cloves) is obtained, consisting of eugenic acid and a hydrocarbon isomeric with oil of turpentine. To separate these substances, the oil is treated with potash, which dissolves the eugenic acid, and the liquid is distilled, whereupon the hydrocarbon passes over, and from the residual eugenate of potassium, eugenic acid may be separated by a mineral acid. The acid may be obtained in like manner from the oil of cinnamon leaves. (Stenhouse.)

Eugenic acid, when purified by distillation, is a colourless oil, of specific gravity 1.076 (Stenhouse); 1.0684 at 4° C. (Williams). It reddens litmus, has a spicy burning taste, and a strong smell of cloves. In contact with air it quickly becomes resinous. It boils at 242° C. (Stenhouse); 251° (Williams). Vapour-density = 6.4 (Dumas); calc. (2. vol.) = 5.68.

Eugenic acid, when exposed to the air, quickly assumes a darker colour, and becomes resinous. By distillation over anhydrous baryta, it is converted into a neutral oil, having the same composition and vapour-density as the acid itself (Calvi, Ann. Ch. Pharm. xcix. 242). According to Church (Phil. Mag. [4] ix. 256), it forms a hydrocarbon boiling at 142° C., and probably consisting of  $C^9H^{12}$ , isomeric with cumene and mesitene. Nitric acid decomposes eugenic acid, forming a brown resin and oxalic acid. With pentachloride of phosphorus, it evolves a gas burning with a green flame like chloride of methyl.

Eugenic acid absorbs the vapour of cyanic acid in large quantity, forming eugen-allophanic acid,  $C^{10}H^{12}O^2.2CNHO$ . (Baeyer, i. 134.)

The chlorides of benzoyl, anisyl, cumyl, and toluyl dissolve in eugenic acid in the cold without alteration; but on heating the liquid, hydrochloric acid is given off in large quantity, and on treating the brown syrupy or solid residue with dilute potash, double anhydrides of eugenyl and the radicle of the chloride are obtained, which may be purified by washing with water and recrystallisation from alcohol; e. g. with chloride of benzoyl:



**Eugenates.** Eugenic acid is monobasic, the general formula of its salts being  $C^{10}H^{11}MO^2$ . The ammonium-salt separates in the granular form from a solution of the acid in aqueous ammonia. The barium-salt crystallises in thin nacreous needles or laminae soluble in alcohol. The calcium-salt forms yellowish micaceous laminae. A basic lead-salt,  $Pb^2O.2C^{10}H^{11}PbO^2$  (?), is obtained as a yellow tenacious precipitate on mixing a solution of a lead-salt with eugenic acid. An acid potassium-salt,  $C^{10}H^{11}KO^2$ .  $C^{10}H^{12}O^2 + aq.$ , according to Brüning (Ann. Ch. Pharm. civ. 202), is obtained by saturating the acid with caustic potash; it forms nacreous needles, which dissolve in water with decomposition and separation of part of the acid; alcohol dissolves it without decomposition. The magnesium-salt is amorphous and insoluble in water. The sodium-salt forms warty crystals having a silky lustre. The strontium-salt resembles the barium-salt.

*Eugenate of Ethyl.*  $C^{12}H^{16}O^2 = \begin{matrix} C^{10}H^{11}O \\ C^2H^5 \end{matrix} \bigg\} O$ . *Eugenethyl, Eugenic ether.*—Obtained by saturating the alcoholic solution of eugenic acid with hydrochloric acid, or by decomposing eugenate of potassium with iodide of ethyl in close vessels. After washing with dilute potash and drying over chloride of calcium, it forms a neutral, colourless, aromatic liquid, insoluble in water, easily soluble in alcohol and ether, boiling at about 240° C.—decomposed by chlorine, bromine, and nitric acid.

**EUGENIN.** *Clove-camphor. Stearoptene of oil of cloves.*—A crystalline substance deposited from water which has been distilled from cloves (*Eugenia caryophyllata*, L.). It was discovered in 1834 by Bonastre (J. Pharm. xx. 565), and according to Dumas is isomeric with eugenic acid; but its molecular weight has not

been determined. It forms white, nacreous laminae, having a faint taste and smell of cloves; insoluble in water, but soluble in all proportions in alcohol and ether. Nitric acid turns it blood-red.

**EUGENO-BENZOIC ANHYDRIDE.**  $C^{11}H^{10}O^2 = \frac{C^{10}H^{11}O}{C^9H^9O}\}O$ . *Benzoeugenyl, Eugenobenzoyl.* (Formation, p. 604.)—After purification by recrystallisation and distillation, it forms colourless needle-shaped crystals, perfectly neutral, insoluble in water, moderately soluble in hot alcohol and in ether. Melts between  $50^\circ$  and  $55^\circ$  C., and boils above  $360^\circ$ . It is not decomposed by boiling aqueous potash, but by fusion with solid potash, it is converted into benzoate and eugenate of potassium. Bromine and nitric acid decompose it more readily, probably forming substitution-products. (Cahours.)

**EUGENOL.** Syn. with EUGENIC ACID.

**EUGENO-CUMINIC ANHYDRIDE.**  $C^{20}H^{22}O^2 = \frac{C^{10}H^{11}O}{C^{10}H^{11}O}\}O$ . See CUMIN-EUGENIC ANHYDRIDE (p. 180).

**EUGENO-TOLUYLIC ANHYDRIDE.**  $C^{11}H^{10}O^2 = \frac{C^{10}H^{11}O}{C^9H^9O}\}O$ . *Tolueugenol.*—Resembles the benzoic compound. Dissolves easily in hot alcohol, and especially in ether. (Cahours.)

**EUGLENA VIRIDIS.** The granules found in these infusoria consist, according to Gottlieb, of paramylum. (See STARCH.) The green colouring matter is insoluble in water, easily soluble in alcohol and ether, somewhat soluble in alkaline liquids. The ethereal solution produces a very strong blood-red dispersion, both of daylight and candle-light. It appears to be different from the chlorophyll of phanerogamous plants, green mosses, and algae. (Salm-Horstmar, Pogg. Ann. xxvii. 331.)

**EULALITE.**  $AgCu^2Se$  or  $\frac{Ag}{Cu}$ Se.—Native selenide of silver and copper, found in a magnesian serpentine rock, intergrown with calcespar, in an abandoned copper mine at Småland in Sweden. It is soft, slightly ductile, with a fine-grained fracture. Colour lead-grey; yields a grey powder and a shining streak. On charcoal before the blowpipe it melts, gives off a strong odour of selenium, and yields a grey, soft, but brittle metallic bead. Colours fluxes like copper. With hot nitric acid it forms a solution from which water throws down selenite of silver. Gives by analysis 23.06 per cent. copper, 38.93 silver, 26.0 selenium, and 8.9 earthy matter. (Berzelius, Schw. J. xxiii. 477.)

**EULAMPHITE.**  $2Al^2HO^2.3M^2SiO^2$  or  $(M^2a^2)SiO^4 + \frac{1}{3}$  aq. (where M represents Mg, Fe, and a small quantity of Mn).—A mineral resembling chlorite in external appearance, found in the granite near Presburg in Hungary. It forms dark green nacreous laminae, cleaving easily parallel to the base, thin cleavage laminae exhibiting a brown or red translucence; soft and flexible. Hardness = 2; specific gravity = 2.73. When strongly heated in a glass tube, it exfoliates and gives off water. Before the blowpipe it melts on the edges to a black magnetic glass; gives the reactions of iron, silicon, and manganese with borax and phosphorus-salt, and dissolves in hydrochloric acid with separation of gelatinous or scaly silica. (Kenngott, Handw. d. Chem. ii. [3] 951.)

**EUKLASE.** Syn. with EUCLASE.

**EUKOLYTE.** A mineral from Brevig, in Norway, closely resembling eudialyte, and regarded by some mineralogists as identical therewith. The two minerals have the same form and nearly the same colour, lustre, and hardness, and agree nearly in composition; but eukolyte is distinguished by the presence of cerium, and, so far as the analysis can be trusted, by a rather larger amount of silica; it has also a browner colour, a somewhat higher specific gravity = 3.0, exhibits more distinct prismatic cleavage, and is especially distinguished by its optical properties, exhibiting negative double refraction, whereas eudialyte is positive. (Kenngott, Handw. ii. [3] 947.)

The following are analyses of eukolyte: a. by Scheerer (Pogg. Ann. lxi. 222; lxxiii. 565); b. by Damour (Compt. rend. xliii. 1197).

	SiO <sup>2</sup>	ZrO <sup>2</sup>	TaO <sup>2</sup>	CeO	LaO	FeO	MnO	CuO	NaO	Cl	Loss by ignition.
a. 47.85	14.05		2.98			7.42	1.94	12.06	12.31	..	0.94 = 99.55
b. 45.70	14.22	2.35	2.32	1.11	6.83	2.35	9.66	11.59	1.11	1.83	= 99.07

Scheerer's analysis leads to the formula  $2M^2O.3SiO^2 = M^4SiO^4.2SiO^2$ ; Damour's to  $3M^2O.5SiO^2 = 3M^4SiO^4.2SiO^2$ , the silicon being replaced to a considerable extent by zirconium (*Rammelsberg's Mineralchemie*, p. 894).



**EUKOLITE-TITANITE.** A mineral occurring, together with eukolite, in the zircon-syenite of Brevig in Norway. It exhibits the colour and lustre of eukolite, but in crystalline form and density, = 3.57, it resembles titanite. Before the blowpipe it exhibits the reactions of silica, ferric oxide, titanite acid, and soda. It is less hard than titanite, and appears to occupy an intermediate place between titanite and eukolite. (Scheerer, Jahresber. d. Chem. 1854, p. 853.)

**EULYSIN.** A name applied by Berzelius to a substance easily soluble in alcohol which he obtained by the action of alcoholic potash on that portion of the alcoholic extract of bile which is soluble in ether: it was probably impure cholelithic acid.

**EULYSITE.** A kind of rock which forms layers in the gneiss of Sweden. It is a granular mixture of augite (probably diallage), garnet, and nearly 50 per cent. of a mineral allied to olivine, being likewise a basic silicate in which the greater part of the magnesia is replaced by protoxide of iron or manganese. When the rock is treated with hydrochloric acid, the last-mentioned mineral is decomposed, with separation of gelatinous silica, while the granules of augite and garnet fall to the bottom. (A. Erdmann, Jahresber. d. Chem. 1849, p. 799.)

**EULYTE and DYSLYTE.** Two crystallisable substances of unknown composition produced, together with others, by the action of strong nitric acid upon citraconic acid: they are distinguished by their different degrees of solubility in water and in alcohol, *eulyte* being the more, *dyslyte* the less soluble. (Baup, Ann. Ch. Pharm. lxxxi. 96.) See CITRACONIC ACID (i. 992).

**EULYTIN.** Silicate of Bismuth. Bismuth-blende.—A rare mineral, occurring at Schneeberg in Saxony, in hemihedral forms of the regular system, the observed faces being  $O$ ,  $\infty O\infty$  and  $\pm \frac{202}{2}$ . The crystals are usually small and often with rounded

edges. Cleavage dodecahedral, very imperfect. Twin-crystals also occur having their plane of composition parallel to a dodecahedral face. The mineral is sometimes also globular, columnar, lamellar, or granular. Hardness = 4.5 to 5.0. Specific gravity = 5.9 to 6.0. Colour brown, yellow, and yellowish-white. Lustre resinous or adamantine. Subtransparent to opaque. Streak yellowish-green or uncoloured. Fracture uneven. Rather brittle. Before the blowpipe it melts easily with intumescence to a brown bead, with brown deposit on the charcoal; with soda it yields metallic bismuth, and with phosphorus-salt a skeleton of silica. Soluble in hydrochloric acid, with separation of gelatinous silica. According to an analysis by Kersten (Pogg. Ann. xxvii. 81), it contains 69.38 per cent.  $\text{Bi}^2\text{O}^3$ , 2.40  $\text{Fe}^2\text{O}^3$ , 0.30  $\text{Mn}^2\text{O}^3$ , 22.23  $\text{SiO}^2$ , 3.31  $\text{P}^2\text{O}^5$ , 2.38 water, together with a small quantity of fluorine, whence it appears to be a silicate of bismuth mixed with a small quantity of ferric phosphate.

**EUMANITE.** A brown variety of titanite anhydride, from Chesterfield in Massachusetts, agreeing in crystalline form with Brookite, and probably identical therewith. Hardness = 6.0. (C. Shepard, Sil. Am. J. xii. 211.)

**EUODYL.**  $\text{C}^{11}\text{H}^{21}\text{O}$  (from *εὐόδινος*, sweet-tasting); sometimes improperly written *euodyl*. An acid radicle, homologous with acetyl, the hydrogen compound of which, euodic aldehyde,  $\text{C}^{11}\text{H}^{21}\text{O.H}$ , is, according to Greville Williams (Proc. Roy. Soc.), the essential constituent of oil of rue. (See RUE, OIL OF.)

**EUONYMIN.** A bitter resinous substance obtained from the oil of the spindle-tree, *Euonymus europæus*. It is insoluble in water, soluble in alcohol and ether, and separates from the latter in warty crystals; it does not however appear to have been obtained pure. (Riederer, Buchn. Repert. xiv. 1.—Grundner, *ibid.* xcvii. 315.)

**EUONYMITE.**  $\text{C}^8\text{H}^{10}\text{O}^6$ . (Kubel, J. pr. Chem. lxxv. 372.)—A saccharine substance obtained from the *cambium* (the viscid secretion which exists in the spring between the bark and the wood) of the branches of the spindle-tree. The cambium of the thicker branches is exhausted with strong alcohol, and on evaporating the solution, euonymite is obtained in highly lustrous monoclinic crystals. It melts at  $182^\circ\text{C}$ . It is isomeric with mannite, and agrees with that substance in most of its properties; but is distinguished by its crystalline form and higher melting point, mannite being trimetric and melting at  $166^\circ\text{C}$ . Gilmer (Ann. Ch. Pharm. exxiii. 375) regards it as identical with dulcite.

**EUPATORIUM.** The water-hemp, *Eupatorium cannabinum*, contains, according to Righoni (Mag. Pharm. xxv. 98), an alkaloid, called eupatorine, having a bitter, rather pungent taste, insoluble in water, soluble in alcohol and ether, and forming a crystallisable sulphate.

The root of the same plant contains, according to Boudet, a volatile oil, a bitter acid substance, starch, and the other ordinary constituents of plants.

**EUPHORBIA.** The roots of *Euphorbia Cyparissias*, *E. Esula*, *E. Lathyris*,



*E. Apios* and *E. depauperata* are emetic and purgative; so likewise is the fixed oil obtained from the seeds of several species, especially of *E. Cyparissias*, *E. Lathyris*, *E. hyberna* and a few others. The seed-oil of these plants may be used in the same way as croton-oil, which is itself the produce of a euphorbiaceous plant. The seeds of *E. Cyparissias* gathered in Auvergne, yielded 6 per cent. fixed oil; those of *E. hyberna* yielded, by exhaustion with ether, 44 per cent. of a golden-yellow fixed oil, having a pleasant and not acrid odour. (Chevallier and Aubergier, J. Chim. méd. viii. 671.)

The milky juice contained in the leaves and stems of euphorbias, is sometimes used as a remedy against the bites of serpents and in syphilis; it is also said to remove warts, especially that of *E. Cyparissias*, *E. Esula*, *E. hypericifolia*, and *E. Tiruculli*. The milky juice of *E. myrtifolia* is peculiarly poisonous. It contains, according to Ricord-Madianna, a non-volatile poisonous principle, euphorbine.

The herb of *E. colonifolia* suspended in water is said to intoxicate fish.

*E. Cyparissias*, a very common weed, contains, according to Riegel (J. pr. Pharm. vi. 165), an organic base, and a peculiar acid, euphorbic acid, forming a crystalline lead-salt, from which the acid may be separated by sulphuretted hydrogen in white needle-shaped crystals. It forms crystallisable salts with the alkalis, and its aqueous solution is precipitated by baryta-water, by acetate of lead, either neutral or basic, and by silver and mercury-salts. Gmelin (*Handbook*, x. 207) regards this acid as identical with malic acid. According to Dessaignes (J. Pharm. [3] xxv. 25), it is a mixture of malic and citric acids with a coloured acid, which precipitates gelatin and copper-salts and blackens iron-salts.

According to Stickel (Arch. Pharm. xl. 30), *E. Cyparissias* and *E. Esula*, also a common weed, contain, besides resin, gallic acid, &c., a white, volatile, crystalline, camphor-like body, having a burning taste and separating gradually from the alcoholic solution, and a yellow colouring matter, which is precipitated by stannous chloride or lead-salts from the extract prepared with water containing alum.

**EUPHORBIC ACID.** } See EUPHORBIA.

**EUPHORBINE.**

**EUPHORBIN.** See EUPHORBICUM.

**EUPHORBICUM.** *Resina s. Gummi Euphorbiæ*. A resin, sometimes improperly called a gum or gum-resin, consisting of the concrete juice of several species of euphorbia, growing in Egypt, Arabia, the Canaries, and other hot countries, either exuding naturally, or from incisions made in the bark. Much of the article found in British commerce is obtained from *Euphorbia canariensis*, while that which occurs on the Continent is obtained from *E. officinarum*, *E. antiquorum*, and other African species, particularly from an undescribed species, called by the Arabs *dergmuse*.

Euphorbium is a variable mixture of resin with wax, caoutchouc, salts, chiefly malates, and from 10 to 20 per cent. of moisture. These constituents may be separated by treating it successively with water, and with cold and hot alcohol.

But even the resin of euphorbium, separated from the wax and other matters, is itself a mixture of three, if not of a greater number of resinous bodies. Berzelius distinguished three resins,  $\alpha$ ,  $\beta$ , and  $\gamma$ . On mixing the alcoholic solution of euphorbium-resin with alcoholic sugar of lead, a precipitate is formed from which, by means of hydrochloric acid and alcohol, a dark-brown resin, the  $\alpha$ -resin, may be separated: it has a sharp burning taste, and dissolves in alkalis and in alcohol.

The liquid filtered from the lead-precipitate yields, when mixed with sulphuric acid, and then with water, a precipitate of the  $\beta$ -resin, easily soluble in alcohol, but insoluble in pure ether. On evaporating the alcoholic solution, this resin remains as a shining, brittle, transparent mass, soluble in very dilute alkalis, and in dilute aqueous acids; hence Buchner and Herberger (Buchn. Repert. vi. 146) regarded it as a base, which they called euphorbiine.

Johnston (J. pr. Chem. xxvi. 145), and H. Rose (Pogg. Ann. xxxiii. 33; liii. 365), have obtained from euphorbium several easily soluble resins.—By exhausting the euphorbium with cold alcohol, a pale yellow solution is obtained, which, when evaporated, leaves a brown-red, brittle, and friable resin,  $C^{20}H^{30}O^4$ , insoluble in caustic alkalis, dissolving with red colour in strong sulphuric acid, and separated unchanged by water.

When euphorbium, after exhaustion with cold alcohol, is well boiled with alcohol, the liquid deposits, on cooling, the  $\gamma$ -resin of Berzelius in indistinct crystals, the composition of which appears to be  $C^{20}H^{22}O^2$ . It is a perfectly indifferent body; its alcoholic solution is not precipitated by ammonia, neutral acetate of lead, nitrate of silver, or by alcoholic potash; but aqueous potash precipitates it. By dry distillation it yields a viscid distillate having an alkaline reaction.

Euphorbium, when swallowed in small doses, produces vomiting and purging; in larger doses it is poisonous. When applied externally it produces irritation, and is therefore employed as an ingredient of vesicating unguents and plasters; but its use is now almost wholly confined to veterinary practice. (Handw. d. Chem. ii. [3] 954.)

**EUPHOTIDE.** Syn. with GABRO.

**EUPHRASIA.** The green parts of *Euphrasia officinalis* (eye-bright), contain, according to Enz (Vierteljahrsschrift pr. Pharm. viii. 175), tartaric, citric, acetic, and lactic acids, red and yellow colouring matter, fixed and volatile oil, and a tannic acid supposed to be peculiar to the plant, and called euphrasia-tannic acid; its lead-salt is said to contain  $3PbO.C^{22}H^{28}O^{17}$ .

100 pts. of the fresh plant, at the flowering time, contained 62.0 pts. water; from the residue, ether dissolved 4.4 pts.; alcohol then 12 pts., water 6.4 pts., and hydrochloric acid 4.4 pts., leaving 10.8 pts. of insoluble residue.

**EUPHYLLITE.** A sub-species of mica allied to Margarodite, occurring, together with corundum and black tourmalin, at Unionville, Delaware County, Pennsylvania. It is greyish or sea-green, with faint mother-of-pearl lustre on the outside, but on the cleavage-faces, which are very perfect, it is white, with very strong nacreous lustre. The laminae are very brittle and perfectly transparent. Hardness 3. Specific gravity 2.963. Before the blowpipe it exfoliates, shines more brightly than emerylite or corundelite and melts on the edges.—The composition of this mineral is variously stated by different analysts. According to Smith and Brush (Sill. Am. J. [2] xi. 209), it contains (mean of four analyses):

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sup>2+</sup> O <sub>3</sub>	Ca <sup>2+</sup> O	Mg <sup>2+</sup> O	K <sub>2</sub> O	Na <sub>2</sub> O	H <sub>2</sub> O
40.28	42.08	1.42	1.25	0.70	3.60	4.71	5.55 = 99.59;

whence the formula  $2M^{2+}O.SiO_2 + 2(3M^{4+}O^2.4SiO_2) + 4aq.$ , which, by reducing the sesquioxides to protoxides, may be converted into that of a combination of an orthosilicate and a hydrate, viz.  $9R'SiO_4.4RHO + 2aq.$

**EUPIONE.** A hydrocarbon, discovered by Reichenbach (Ann. Ch. Pharm. xiii. 217), and consisting essentially, according to Frankland, of hydride of amyl,  $C^5H^{12}$ . It is produced by the dry distillation of many organic bodies, viz. of wood, coal, fixed oils, caoutchouc, resin, bones, &c.; it is, therefore, a constituent of wood-tar, and, in greater abundance, of coal-tar, but is found most abundantly in rectified bone-oil (i. 625), and in the oil obtained by the dry distillation of rape-seed and hemp-seed. According to Hesse (Ann. Ch. Pharm. xxiii. 247), it does not exist in the crude empyreumatic oils obtained from these several sources, but is produced in the process of purifying them by the action of sulphuric acid. To prepare it from rectified bone-oil, the oil is mixed with  $\frac{1}{2}$  of its weight of oil of vitriol; the lighter and clearer liquid, which rises to the surface, is taken off and distilled with an equal weight of sulphuric acid and a small quantity of nitre; the distillate is again distilled with sulphuric acid, then washed with aqueous potash and with water, rectified, dried under the air-pump, and treated with potassium as long as the metal shows signs of oxidation.

Eupione is a colourless, extremely mobile liquid, having a very low refracting power. It is tasteless, and has an agreeable odour, like that of flowers. It does not conduct electricity. Specific gravity = 0.65 at 20° C. It remains liquid at 20° C., expands very much when heated, 100 vol. at 20° C. expanding to nearly 104.5 vol. at 47° C. It is very volatile, evaporating perceptibly at common temperatures. When dropped on paper, it makes a grease-stain, which quickly disappears; it evaporates instantly on the skin, boils at 47° C., and distils unaltered. It is inflammable, and burns with a smokeless flame.

Eupione is insoluble in water, sparingly soluble in aqueous alcohol, but mixes easily with absolute alcohol, ether, and oils both fixed and volatile. It dissolves sulphur and phosphorus only with aid of heat; many fats, camphor, and similar substances with facility, caoutchouc also when heated, the solution leaving a dry varnish when evaporated. Resins it dissolves for the most part with difficulty and incompletely; and most alkaloids are quite insoluble in it, even at the boiling heat.

Eupione is a very stable substance; it is not altered by light; sulphuric acid, nitric acid, alkalis, potassium, and sodium have no action upon it, and even permanganate of potassium is said not to be reduced by it. With chlorine, bromine, and iodine, it unites without undergoing decomposition.

**EUPYRCHROITE.** A native phosphate of calcium (phosphorite) occurring in large quantity at Crown Point, New York, and used abundantly as manure. (See PHOSPHORITE.)

**EURITE.** A variety of syenite occurring near Christiania; it is of a blue colour and stratified. Two specimens gave:

SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O	Ca <sup>2</sup> O	Mg <sup>2</sup> O	K <sup>2</sup> O	Na <sup>2</sup> O	H <sup>2</sup> O	FeS <sup>2</sup>
53.85	15.43	9.30	6.73	1.14	3.40	4.36	2.32	0.785 = 97.315
58.50	18.14	7.07	2.89	1.51	2.36	5.53	3.45	trace = 99.45

(Kjerulf, Jahresber. d. Chem. 1854, p. 882.)

**EUSYNCHITE.** Vanadate of lead, found in abandoned workings, at Hofgrund near Freiburg, in the Breisgau. It is micro-crystalline, and forms spherical or botryoidal aggregates and crusts of yellowish-red or leather-yellow colour, with somewhat lighter streak; scarcely translucent on the edges; distinctly radio-fibrous. Hardness = 3.5. Specific gravity = 4.945. Melts to a lead-grey bead before the blow-pipe; yields lead on charcoal, and with phosphorus-salt, a yellow bead in the oxidising, green in the reducing flame; gives by analysis 55.70 Pb<sup>2</sup>O; 20.49 VO<sup>2</sup>; 22.69 VO<sup>3</sup>; 0.94 SiO<sup>2</sup> (total 99.82). (Fischer and Nessler, Jahresber. d. Chem. 1855, p. 964.)

**EUTOMITE.** See TELLURIC BISMUTH.

**EUXANTHIC ACID.** C<sup>2</sup>H<sup>10</sup>O<sup>11</sup>. *Purreic acid.* (Stenhouse, Ann. Ch. Pharm. li. 423.—Erdmann, J. pr. Chem. xxxiii. 190; xxxvii. 385.)—This acid, in combination with magnesia, constitutes the essential part of purree or Indian yellow, a substance imported into Europe from India and China, and consisting, according to most authorities, of the dried sediment of elephants' or buffaloes' urine; but, according to Stenhouse, of a vegetable extract, obtained by evaporating down the juice of certain plants mixed with magnesia. (See PURREE.)

To prepare euxanthic acid, the purree is exhausted with boiling water, and the residue is dissolved in boiling dilute hydrochloric acid. The solution on cooling deposits euxanthic acid in yellowish needles grouped in stars. It is sparingly soluble in cold water, but dissolves easily in alcohol and ether. When crystallised from alcohol it retains 1 at. water (C<sup>2</sup>H<sup>10</sup>O<sup>11</sup>.H<sup>2</sup>O), and when precipitated by hydrochloric acid from its ammoniacal solution, 3 at. water (C<sup>2</sup>H<sup>10</sup>O<sup>11</sup>.3H<sup>2</sup>O). This water of crystallisation (4 or 11 per cent.) is given off at 130° C. The acid has a sweet taste, with bitter after-taste. It is coloured deep yellow by alkalis.

Euxanthic acid cautiously heated in a tube yields a yellow sublimate of euxanthone; C<sup>2</sup>H<sup>10</sup>O<sup>11</sup> = C<sup>2</sup>H<sup>2</sup>O<sup>2</sup> + CO<sup>2</sup> + 3H<sup>2</sup>O. The same substance is produced by the action of strong sulphuric acid, together with hamathionic acid, C<sup>1</sup>H<sup>4</sup>SO<sup>12</sup>.

With chlorine, bromine, and cold nitric acid, euxanthic acid forms substitution-products (p. 610). Hot nitric acid converts it into coccinonic acid, together with oxalic acid, and ultimately into oxypicric or styphnic acid.

**Euxanthates.** Euxanthic acid is monobasic, the general formula of its salts being C<sup>2</sup>H<sup>11</sup>MO<sup>11</sup>. The euxanthates of the alkali-metals are soluble in water. The barium- and calcium-salts dissolve sparingly in cold, easily in boiling water; the neutral magnesium-salt is also soluble, but the basic salt contained in Indian yellow is insoluble. The other salts are sparingly soluble or insoluble in water.

*Euxanthate of ammonium*, C<sup>2</sup>H<sup>11</sup>(NH<sup>4</sup>)O<sup>11</sup>, crystallises in light yellow, highly lustrous needles. The *potassium-salt* crystallises from a warm solution of euxanthic acid in acid carbonate of potassium, in light yellow crystalline scales. The *neutral lead-salt*, C<sup>2</sup>H<sup>11</sup>PbO<sup>11</sup>, is precipitated from the aqueous solution of the ammonium-salt by neutral acetate of lead in yellow flocks. The *basic lead-salt*, PbO.2C<sup>2</sup>H<sup>11</sup>PbO<sup>11</sup> + aq., is thrown down from a boiling alcoholic solution of euxanthic acid by an alcoholic solution of basic acetate of lead, as a yellow precipitate.

*Euxanthate of Magnesium.*—On adding euxanthate of ammonium and a little free ammonia to a solution of chloride of magnesium containing sal-ammoniac, a yellow amorphous precipitate is formed, which dissolves in boiling water, but soon separates as an orange-coloured jelly, which changes on standing into a shining yellow crystalline powder, no longer soluble in water, and consisting of a basic salt, probably MgO.2C<sup>2</sup>H<sup>11</sup>MO<sup>11</sup> + 8 aq. This salt forms the chief constituent of Indian yellow; in the pure state, however, it has a much finer colour than the pigment so called, which contains a larger and variable quantity of magnesia. Erdmann, indeed, found 46 per cent. magnesia in Indian yellow, whereas the pure salt obtained as above contains only 9.5 per cent.

*Euxanthate of silver* is a gelatinous yellowish precipitate, somewhat soluble in water, and turning brown when exposed to light.

A solution of euxanthate of ammonium forms with *ferric* salts, a blackish-green precipitate; with *ferrous* salts, dark green (Stenhouse); white becoming dark-coloured by contact with the air (Erdmann); with *cupric* salts, a stiff yellow jelly, somewhat soluble in pure water; with *manganous*, *nickel*, and *zinc* salts, lemon-yellow precipitates; with *mercuric chloride*, after some time, a slight yellowish precipitate.



*Derivatives of Euxanthic acid.*

**Bromeuxanthic acid**,  $C^{21}H^{16}Br^2O^{11}$ , is obtained by the action of bromine on euxanthic acid in presence of water. It is soluble in boiling alcohol, which on cooling deposits it in golden-yellow microscopic needles. The mother-liquor, when evaporated, yields an additional quantity of the acid in the amorphous state, the amorphous modification being much more soluble in alcohol than the crystalline acid.

The salts of bromeuxanthic acid are gelatinous; the potassium- and ammonium-salts however exhibit, after a while, a tendency to crystallise in needles.

**Chloreuxanthic acid**,  $C^{21}H^{16}Cl^2O^{11}$ , is obtained by passing chlorine into water in which euxanthic acid is suspended. It crystallises in shining golden-yellow scales, insoluble in water, easily soluble in boiling alcohol, sparingly in cold alcohol. Its salts are mostly gelatinous.

**Nitroeuxanthic acid**,  $C^{21}H^{16}(NO^2)^2O^{11}$ .—Obtained by immersing euxanthic acid in cold nitric acid of specific gravity 1.31. It dissolves sparingly in water and in cold alcohol, easily in boiling alcohol, whence it crystallises in straw-coloured laminae. Its salts are mostly gelatinous, and deflagrate when heated.

**Coccinonic acid**. *Nitrococcinonic acid* of Berzelius.—This acid was discovered by Erdmann, who assigned to it the formula  $C^{22}H^{17}(NO^2)O^2$ ; according to Laurent, it is perhaps *nitroquinonic acid*,  $C^{22}H^{17}(NO^2)O^2$ , or  $C^6H^5(NO^2)O^2$ . It is produced, together with oxalic acid, when euxanthic acid is heated with nitric acid of specific gravity 1.31, and separates as the liquid cools. If the heat is not strong enough, nitro-euxanthic acid is formed at the same time; in that case, the filtrate when heated will yield an additional quantity of coccinonic acid.

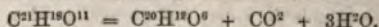
This acid forms yellow crystalline grains, which become strongly electric by friction. It is especially distinguished by its property of forming, with bases, scarlet salts which burn with slight detonation. The ammonium-salt is soluble in water and in excess of carbonate of ammonia. The potassium-salt is sparingly soluble in water and in excess of carbonate of potassium.

By the continued action of nitric acid, coccinonic acid is converted into oxypicric acid.

**Hamathionic acid**.—A product of the action of sulphuric acid on euxanthic acid. Its composition is not quite determined. Erdmann, who discovered it, assigned to it the formula  $C^{14}H^7O^{13}S$  or  $C^{14}H^7O^{12}.SO^2$ . A solution of euxanthic acid in cold sulphuric acid yields, on addition of water, a precipitate of euxanthone, and if the filtrate be saturated with carbonate of barium or oxide of lead, filtered from insoluble salt, and the pale yellow liquid carefully evaporated out of contact with the air, a strongly acid solution of free hamathionic acid is obtained, which dries up to a syrup by evaporation at a low temperature, but is decomposed by boiling, with elimination of sulphuric acid.

The hamathionates of the alkali-metals of barium and of lead dry up to yellowish gummy masses. The solutions decompose in contact with the air, with separation of a brown powder and liberation of sulphuric acid. The solution of the neutral lead-salt yields, on addition of basic acetate of lead, a yellow precipitate chiefly consisting of triplumbic hamathionate.

**EUXANTHONE**,  $C^{20}H^{12}O^6$ . *Purrenone* (Stenhouse), *Porrone* (Berzelius).—A neutral product of the decomposition of euxanthic acid, first obtained by Stenhouse (Ann. Ch. Pharm. li. 425), and soon afterwards by Erdmann (*ibid.* lii. 365; lx. 289). It is produced by heating the acid, or its barium- or lead-salt *per se*; or by treating the dry acid with strong sulphuric acid; or its alcoholic solution with hydrochloric acid gas. The transformation may be represented as follows:



In preparing euxanthone by the action of heat on euxanthic acid, or its barium- or lead-salt, it is best not to raise the temperature to the subliming point of euxanthone, but to keep it between  $160^\circ$  and  $180^\circ$  C. The euxanthone then remains in the residue, and may be freed from undecomposed euxanthic acid by digestion with ammonia, and then recrystallised from alcohol.

Euxanthone forms pale yellow shining needles or laminae, slightly soluble in water and in cold alcohol. When carefully heated it sublimes for the most part without decomposition. It is perfectly neutral, dissolves in strong aqueous ammonia, and easily in potash, but not in dilute acids. The alcoholic solution is precipitated by basic acetate of lead, but not by the neutral acetate, or by baryta or lime. Nitric acid decomposes it, producing first porphyric acid,  $C^{13}H^8(NO^2)^3O^4$  [?], then oxyporphyrin acid,  $C^{13}H^8(NO^2)^2O^4$ , and lastly oxypicric or styphnic acid,  $C^6H^5(NO^2)^2O^4$ .

Chlorinated and brominated derivatives of euxanthone are produced, not by the

direct action of chlorine and bromine on euxanthone, but by dissolving chloreuxanthic and bromeuxanthic acid in strong sulphuric acid, and precipitating by water. The mother-liquor retains an acid containing chlorine or bromine, and sulphuric acid, and forming a soluble barium-salt [? chlor- or brom-hamathionic acid], but no hydrochloric acid.

*Chloreuxanthone* separates from its alcoholic solution in yellow feathery crystals containing  $C^3H^3Cl^3O^4$ . The formation of this trichlorinated compound from dichloreuxanthic acid seems to show that the composition of euxanthone is not adequately expressed by the formula  $C^3H^{12}O^4$ , and that its formation from euxanthic acid is not quite so simple as it is represented by the equation above given (p. 610).

*Bromeuxanthone* is precipitated by water as a pulverulent substance; it is probably analogous in composition to chloreuxanthone, but it has not been analysed.

**EUXENITE.** A mineral consisting mainly of niobate and titanate of yttrium, found at Stromoe, near Arendal, and other localities in Norway. According to Breithaupt, it forms crystals belonging to the trimetric system; but it is usually massive without trace of cleavage, and with imperfectly conchoidal fracture. Opaque in the mass, translucent in thin splinters. Lustre metallic and waxy. Colour brownish-black. Streak brown. Hardness = 6.5. Specific gravity = 4.6 to 5.0. It is not attacked by acids, is infusible before the blowpipe, gives off water when heated, becomes yellowish-brown on ignition, and forms, with borax and phosphorus-salt, yellow glasses, the latter becoming light green or colourless on cooling.

*Analyses.*—a. Brownish-black, from Jölster (Scherer, Pogg. Ann. l. 149), approximate analysis; b. Brownish-black from Tvedestrand (Scherer, *ibid.*); c. Black, from Tremoe (Strecker, J. pr. Chem. lxiv. 384). d. Forbes and Dahl (*ibid.* lxvi. 444; lxix. 353):

	NbO <sup>3</sup>	TiO <sup>2</sup>	Al <sup>3</sup> O <sup>3</sup>	U <sup>3</sup> O	Fe <sup>2</sup> O	Y <sup>2</sup> O	Ca <sup>2</sup> O	La <sup>2</sup> O	Ca <sup>2</sup> O	Mg <sup>2</sup> O	H <sup>2</sup> O
a.	49.66	7.94	. .	6.34	. .	25.09	2.18	0.96	2.47	0.29	3.97 = 98.90
b.	53.64	. .	. .	7.58	2.60	28.97	2.91	. .	. .	. .	4.04 = 99.74
c.	37.16	16.26	. .	8.45	3.03	26.46	. .	. .	5.25	. .	2.68 = 99.29
d.	38.58	14.36	3.12	5.22	1.98	29.35	3.31	. .	1.38	0.19	2.88 = 100.37

**MUZOLITE.** Syn. with STILBITE.

**EVAPORATION.** See HEAT.

**EVERNIA.** The lichen known as *Evernia* or *Parmelia prunastri*, contains, according to Rochleder and Heldt (Ann. Ch. Pharm. xlviii. 2), besides fat, cellulose, &c., a chromogen or colour-producing substance, identical with Schunck's lecanoric acid; according to Stenhouse, it contains evernic acid together with usnic acid; according to Hesse, it also contains oxalic acid.

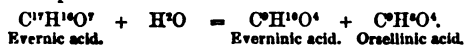
**EVERNIC ACID.**  $C^3H^{10}O^7$ . (Stenhouse [1848], Ann. Ch. Pharm. lxviii. 83).—An acid homologous with lecanoric acid, obtained from *Evernia prunastri*. To prepare it, the lichen is exhausted with milk of lime, the yellowish filtrate is neutralised with hydrochloric acid, and the resulting light yellow flocculent precipitate is washed with water, carefully dried, and then digested at a gentle heat in weak spirit, till about  $\frac{2}{3}$  of it is dissolved (the remainder consisting of usnic acid). The filtrate on cooling deposits evernic acid in yellow crystals, which may be purified by recrystallisation from weak spirit, with addition of animal charcoal.

Evernic acid forms aggregates of small colourless crystals, destitute of taste and odour. It is insoluble in cold, and sparingly soluble in boiling water; easily soluble in alcohol and ether. It melts at 164° C., and decomposes at higher temperatures, yielding orcin and an empyreumatic oil. Solution of hypochlorite of calcium colours it yellowish. The ammoniacal solution absorbs oxygen from the air and acquires a dark red colour.

By the action of potash or baryta-water, evernic acid is resolved into orsellinic and evernicinic acids, the former of which is soon further decomposed into orcin and carbonic anhydride. Evernic acid quickly absorbs bromine. When boiled with alcohol it yields everninate and orsellinate of ethyl, the latter of which quickly undergoes further decomposition.

Evernic acid is monobasic. The barium-salt,  $2C^3H^{10}BaO^7$  + aq., forms small white prismatic crystals, sparingly soluble in cold water, easily in weak spirit. The potassium-salt,  $C^3H^{10}KO^7$ , is colourless, with silky lustre, sparingly soluble in cold water and in aqueous carbonate of potassium, easily in weak spirit and in caustic potash.

**EVERNICINIC ACID,** or *Evernesic acid*.  $C^3H^{10}O^4$ . (Stenhouse, *loc. cit.*)—A product of the decomposition of evernic acid under the influence of caustic alkalis:





The orsellinic acid quickly undergoes further decomposition into carbonic anhydride and orcin, which remains in the mother-liquor.

The best mode of preparing everninic acid is to boil evernic acid with baryta-water. Carbonate of barium is then deposited, and the filtrate treated with hydrochloric or acetic acid, yields a precipitate of everninic acid, which may be purified by boiling with water and animal charcoal (Stenhouse). Everninic acid may also be prepared directly from *Evernia prunastri* containing a large quantity of evernic acid, by boiling the lichen with water, evaporating down the aqueous solution, and mixing it with hydrochloric acid; it then after a while deposits impure everninic acid, which may be purified as above. (Hesse.)

Everninic acid forms crystalline laminae resembling benzoic acid, colourless, tasteless, and inodorous; sparingly soluble in cold, moderately in boiling water, very easily in alcohol and ether. The solutions reddens litmus. The acid melts at  $147^{\circ}\text{C}.$ , and is decomposed at a stronger heat, emitting an agreeable odour (suffocating, according to Hesse), and yielding a white crystalline sublimate.

Everninic acid dissolves easily in cold sulphuric acid; on heating the liquid, carbonisation takes place, with evolution of sulphurous anhydride.

Dilute nitric acid scarcely acts on everninic acid; the concentrated acid decomposes it slowly in the cold, more quickly with aid of heat, forming evernitic acid, together with oxalic acid and other substances not distinctly made out. (Hesse.)

Everninic acid is coloured yellowish by hypochlorite of calcium, like evernic acid; but is distinguished from the latter by not yielding orcin when boiled with potash, and by its ammoniacal solution not turning red on exposure to the air.

Everninic acid is monobasic; a few only of its salts have been prepared. *Everninate of barium*,  $\text{C}^9\text{H}^7\text{BaO} + \text{aq.}$ , is obtained by decomposing evernic acid with baryta-water as above described; the liquid filtered from carbonate of barium is evaporated, freed from orcin and colouring matter by washing with alcohol or ether, and the residue is crystallised from weak spirit. The salt forms long, hard, four-sided prisms; it is nearly insoluble in absolute alcohol, but dissolves in weak spirit.

The *silver-salt*,  $\text{C}^9\text{H}^7\text{AgO}^4$ , is obtained as a white precipitate on adding nitrate of silver to an ammoniacal solution of the acid.

*Everninate of ethyl or Evernic ether*,  $\text{C}^{11}\text{H}^{10}\text{O}^4 = \text{C}^9\text{H}^7(\text{C}^2\text{H}^5)\text{O}^4$ , does not appear to be produced by the action of hydrochloric acid gas on an alcoholic solution of everninic acid, but is obtained from evernic acid (p. 611), by boiling that acid for 8 or 10 hours with strong alcohol, evaporating nearly to dryness, washing with cold water to separate orcin (p. 611), and recrystallising from alcohol with aid of animal charcoal. Or better: evernic acid is dissolved in alcohol, with addition of caustic potash, and the liquid is boiled, neutralised with carbonic acid gas, and evaporated. The dark brown liquid, which still contains orcin, deposits brown crystals of evernic ether, which are purified with alcohol and animal charcoal.

Evernic ether forms long colourless crystals, destitute of taste and odour, insoluble in cold, and nearly insoluble in boiling water, easily soluble in alcohol and ether. It melts at  $56^{\circ}\text{C}.$ , and crystallises on cooling. It dissolves in caustic potash without decomposition; not in ammonia, or in carbonate of potassium.

**EVERNITIC ACID.**  $\text{C}^9\text{H}^7(\text{NO}^2)^2\text{O}^4$ , or  $\text{C}^9\text{H}^7(\text{NO}^2)^2\text{O}^2$  (?). (O. Hesse [1861], Ann. Ch. Pharm. cxvii. 300).—An acid resembling oxypicric acid, produced by the action of nitric acid on everninic acid. This acid, digested at a gentle heat with ten times its weight of strong nitric acid, dissolves with evolution of nitrous acid; and on saturating the brownish yellow solution with carbonate of sodium, evaporating to dryness, exhausting with alcohol, evaporating to expel the alcohol, filtering to separate an amorphous deposit, and mixing the filtrate with nitric acid, needles of evernitic acid are deposited after a few hours, while oxalic acid and other foreign substances remain in solution.

Evernitic acid forms long pale yellow prisms, or a white crystalline powder. It dissolves sparingly in cold, more readily in boiling water, forming a yellow solution, which has an astringent taste, but no acid reaction. It dissolves easily in alcohol, forming an acid solution; it dissolves also in ether. When heated it melts and carbonises, and if quickly heated, decomposes with slight explosion. It colours the skin yellow. Dissolves in nitric acid.

Evernitic acid is dibasic; the alkali-metal salts, which are easily soluble, may be obtained by direct union of the acid with the bases. The *barium-salt* separates, on adding chloride of barium to a solution of the sodium-salt mixed with acetic acid, in brownish yellow needles, which detonate strongly when heated. A lead-salt containing 30 per cent. lead is obtained in like manner by precipitation from an acid solution, in yellow detonating needles.

*Evernitate of potassium*,  $\text{C}^9\text{H}^7\text{K}^2(\text{NO}^2)^2\text{O}^4 + \frac{3}{2}\text{aq.}$ , or  $\text{C}^9\text{H}^7\text{K}^2(\text{NO}^2)^2\text{O}^2 + \frac{1}{2}\text{aq.}$ , is separated from the solution of the acid in potash-ley by carbonic acid, in orange-yellow needles which dissolve with yellow colour in water and alcohol: the aqueous solution



is neutral. The crystals dried over oil of vitriol give off 6·7 per cent. water, and the dried salt gives by analysis 28·8 per cent. carbon, 2·8 hydrogen, and 21·7 potassium; numbers agreeing nearly with either of the preceding formulæ, the first of which requires 28·79 C, 2·66 H, and 20·88 K; the second 29·00 C 2·12 H, and 21·05 K.

**EXANTHALOSE.** Native sulphate of sodium. (See SULPHATES.)

**EXCREMENTS.** The matters discharged from the intestinal canal consist partly of undigested residues of food, partly of certain intestinal secretions, which, after having served their purpose in effecting the digestion of the food, are no longer fit to return into the blood. The excrements have mostly an acid, sometimes, however, a neutral or alkaline reaction.

From the observations of Wehsarg (*Mikroskopische und chemische Untersuchungen der Fæces gesunder erwachsener Menschen*, Giessen, 1853), it appears that a full-grown healthy man discharges on the average, in twenty-four hours, 131 grammes (about 4 oz.) of fæces, containing 26·7 per cent. of solid matter (dried at 120° C.), therefore 35 grammes (about 1 oz.) of solid matter in twenty-four hours.

The solid matter of the excrements consists mainly of insoluble remnants of food, insoluble salts, and sand. The portions soluble in water, alcohol, and ether, contain, though by no means constantly, albuminous matters, volatile fatty acids, among which are butyric and acetic acids, lactic acid, sugar, taurine, resinous products of the decomposition of bile, including choleidic acid and dyslysin, unaltered bile-pigment, but very rarely undecomposed bile (only indeed when the alimentary matters pass rapidly through the intestines, as in diarrhœa or tuberculosis, or when the secretion of bile is abnormally increased, as by the action of calomel),—fat (sometimes in considerable quantity and in masses resembling margarin), excretin and excretolic acid, and small quantities of soluble salts, chiefly alkaline phosphates, with mere traces of sulphates and chlorides, the potassium-salts being more abundant than the sodium-salts. The portion of the excrements insoluble in water, alcohol, and ether contains,—besides food-remnants and sand—earthy and ferric phosphates, and sometimes oxalate of calcium (after the taking of food containing oxalates).

Berzelius (*Lehrbuch*, 4 Aufl. ix. 340—349) found in human fæces :

Water . . . . .	75·3
Bile . . . . .	0·9
Albumin . . . . .	0·9
Peculiar extractive matter . . . . .	2·7
Salts . . . . .	1·2
Insoluble residue of digested aliments . . . . .	7·0
Insoluble matters added in the intestinal canal, mucus, biliary resin, and peculiar animal fat. . . . .	12·0
	100·0

Wehsarg found in 1000 pts. of human fæces, 733 pts. of water and 267 pts. of solid matter, yielding on the average 53·4 pts. of matter soluble in water, 41·6 alcoholic extract, 30·7 ether-extract, 80·0 insoluble food-residues, and 10·95 inorganic salts precipitable by ammonia.

In the ash of human excrement Porter (Ann. Ch. Pharm. lxxi. 109) found :

K <sup>2</sup> O	Na <sup>2</sup> O	Ca <sup>2</sup> O	Mg <sup>2</sup> O	Fe <sup>2</sup> O <sup>3</sup>	P <sup>2</sup> O <sup>5</sup>	SO <sup>3</sup>	CO <sup>2</sup>	NaCl
6·10	5·07	26·46	10·54	2·50	36·03	3·13	5·07	1·33 = 96·23

Fleitmann (Pogg. Ann. lxxv. 356) found in the ash 30·58 per cent. soluble salts. According to Berzelius, human excrements contain relatively less lime and more magnesia than the food; and, according to Wehsarg, they contain only traces of phosphate of calcium, but considerable quantities of phosphate of magnesium. According to Porter's analysis, however, the proportion of lime exceeds that of magnesia. The proportion of soluble salts in the solid excrements is, under normal conditions, very much less than in the urine, and only becomes considerable in diarrhœa, cholera, and other diseases of the intestinal canal.

The following results respecting the constitution of the excrements of man and animals have been obtained by Dr. Marcet (Phil. Trans. 1854, p. 265; 1857, 403). When healthy human fæces are completely exhausted with boiling alcohol, a residue is obtained which is completely insoluble in ether, and from which boiling water extracts nothing but ammonio-magnesian phosphate. The clarified alcoholic solution deposits after long standing a precipitate which appears to contain a peculiar granular substance and an olive-coloured fatty acid, excretolic acid, which melts between 25° and 26° C. The alcoholic solution separated from this deposit and mixed with milk of lime, yields a brown precipitate, from which, after drying, ether extracts a

crystallisable substance, excretin. Marcet is of opinion that human faeces generally contain excretin in the free state. The lime precipitate, freed from excretin by means of ether and treated with hydrochloric acid, yields margaric acid; it likewise contains a colouring matter apparently resembling that of the blood, or that which Harley (Proc. Roy. Soc. vii. 122) has obtained from urine. The amount of margaric acid seems to depend on the quantity of vegetable food. In the acid excrements of a patient in whom the flow of bile into the intestine was obstructed by the pressure of an enlarged and disorganised pancreas, Marcet found acid stearate of sodium, together with considerable quantities of free fatty acids. (Chem. Soc. Qu. J. x. 162.)

The faeces of carnivorous animals contain, not excretin, but a substance resembling it, together with butyric acid; those of the crocodile contain cholesterin, but no uric acid; those of the boa contain uric acid, but no cholesterin; and those of vegetable-feeding animals contain neither excretin, butyric acid, nor cholesterin.

The excrements of birds and serpents, which, mixed with the renal secretion, are discharged from these animals through the cloaca, partake, to a great extent, of the nature of urine, consisting chiefly of alkaline urates and earthy phosphates. (See GUANO and URINE.)

The excrements of insects consist mainly of the remnants of the tissues, animal or vegetable, which they have swallowed as food, mixed with constituents of the urine, if the insect is not provided with special urinary organs.

For further details on excrements, see *Lehmann's Physiological Chemistry*, translated by Day, ii. 141; iii. 517.—*Gmelin's Handbuch*, viii. 93.—*Handw. d. Chem.* ii. [3] 971.

**EXCRETIN.**  $C^{18}H^{16}SO_2$ . (Marcet, *loc. cit.*, also Proc. Roy. Soc., ix. 308.)—This substance crystallises readily from the alcoholic extract of the faeces, in silky crystals, very soluble in ether, sparingly soluble in cold alcohol, insoluble in water. It has an alkaline reaction, and is not decomposed by dilute mineral acids. Melts between  $95^\circ$  and  $96^\circ$  C. Human faeces contain, on the average, 0.46 gm. of impure excretin, and 0.184 gm. of pure excretin in one evacuation. The faeces of a child one year old were found to contain not excretin, but cholesterin.

**EXCRETOLIC ACID.** A fatty acid, obtained by Marcet from the alcoholic extract of human excrements (for the method of obtaining it, see page 613). It has a feculent odour; melts at  $25^\circ$ — $26^\circ$  C.; and when heated on platinum-foil, emits an odour like that of burning excretin, and burns away with a bright flame. It is insoluble in water, soluble in ether, sparingly soluble in cold, easily in hot alcohol. The solution has a distinct acid reaction.

**EXOPHACIN.** The name given by Valenciennes and Frémy to the outer portion of the crystalline lens of the eyes of mammalia.

**EXOSMOSE.** See OSMOSE.

**EXPANSION.** See HEAT.

**EXSICCATOR.** A drying apparatus, consisting of an enclosed space containing substances which rapidly absorb moisture, such as oil of vitriol, dry chloride of calcium, &c.

**EXTRACT.** A pharmaceutical term, applied to the tough or viscid masses, obtained by treating organic substances with solvents, and then evaporating the solvent. (See *Ure's Dictionary of Arts, Manufactures, and Mines*, ii. 167; and *Handwörterbuch der Chemie*, ii. [3] 977.)

**EYE.** The eye consists of three coatings, the sclerotic, choroid, and retina, enclosing the crystalline lens, and two transparent liquids or humours, the aqueous and the vitreous.

The sclerotica is a hard, tough membrane, enveloping the entire globe of the eye, opaque for the most part, but transparent in front: this transparent portion, which is more convex than the rest, is called the cornea.

The sclerotica is composed of a tissue which is converted into chondrin by the action of boiling water, leaving only a small residue of vessels. Boiling hydrochloric acid first contracts and then dissolves it rapidly. Acetic acid converts it into a jelly soluble in water, forming a solution which is not rendered turbid by ferrocyanide of potassium. The sclerotica contains in 100 pts., 51.00 C, 7.08 H, 18.72 N, and 23.20 O. (Scherer.)

The cornea is also composed of tissues which yield chondrin when boiled with water and dissolved in hydrochloric acid. Acetic acid first contracts the cornea and then dissolves it completely. The solution is precipitated by potash, and by ferrocyanide of potassium.

The choroid is a tissue lining the interior of the eye-ball, next to the sclerotic coat; it yields chondrin when boiled with water.

The retina, which is the innermost coating of the eye, is soft and semitransparent,

and approaches in composition to the nerves and brain; it may, indeed, be regarded as an expansion of the optic nerve. It contains, according to Lassaigne, 92·90 per cent. water, 0·85 saponifiable and phosphoretted fat, and 6·25 albumin.

Between the choroid and the retina is interposed a layer of cells filled with a black opaque substance, called the black pigment, the pigmentum nigrum or ophthalmomelanin. When separated by washing from the enclosing membrane, it forms a heavy black powder, perfectly insoluble in water, alcohol, and ether, sparingly soluble or insoluble in dilute mineral acids, but dissolved by caustic potash, with evolution of ammonia. It burns with an unpleasant odour, leaving a small quantity of ash containing iron. The organic matter of the black pigment contains, according to Scherer, 58·0 per cent. C, 6·0 H, 14·0 N, and 22·0 O.

The iris, which is the coloured reticular membrane, situated in front of the eye, just behind the cornea, consists chiefly of fibrin.

The crystalline lens is a transparent body, having the form of a double convex lens, situated behind the pupil. In man and mammiferous animals in general, it consists of fibres, which, in the central portions of the lens, the exophacin, consists of an albuminous substance (*albumin a*), which coagulates at about 65° C., but does not lose its transparency when treated with alcohol, even for a long time. In the outer portion of the lens, the exophacin, the fibres are united by another albuminous substance (*metalbumin*), which does not coagulate at the boiling heat; both these substances differ from ordinary albumin (i. 66), in not forming a blue solution with hydrochloric acid. The crystalline lenses of birds and reptiles differ but slightly from those of mammalia. The crystalline lens of fishes is also formed of two parts, the outer of which (the exophacin) consists of metalbumin, the inner of an albuminous substance, insoluble in water, called *phaconin*. The fibres of the crystalline lens of mammalia exhibit a close resemblance to the phaconin of fishes.

These several albuminous bodies do not differ much in composition, either from each other or from ordinary albumin (i. 67), as the following table will show:—

	Albumin a	Metalbumin.	Phaconin.
Carbon . . . .	51·89 .	52·8 .	52·11
Hydrogen . . . .	6·75 .	7·3 .	7·69
Nitrogen . . . .	15·46 .	16·0 .	16·53
Oxygen . . . .	25·90 .	23·9 .	23·67
	100·00 .	100·0 .	100·00

In the eye of a horse which had become blind by cataract, the albumin and the metalbumin were found to be insoluble in water, and a number of membranes had formed, nearly opaque, and easily separated from one another. These membranes, when incinerated, did not leave a larger proportion of ash than ordinary white of egg. (Valenciennes and Fremy, *Compt. rend.* xliv. 1122.)

The aqueous humour, which fills the space between the cornea and the crystalline lens, is a mobile saline liquid, having a specific gravity of 1·0053, and containing, according to Berzelius, 98·10 per cent. water, 1·15 chloride and lactate of sodium, and 0·75 free soda, besides a small quantity of albumin.

The vitreous humour is a gelatinous liquid, which fills up the entire space behind the crystalline lens. It has a saline taste, is colourless and transparent, but becomes opaline when boiled. It contains 98·40 per cent. water, 0·16 alkaline chlorides and lactates, and 1·42 soda and animal matter (Berzelius). The colour and composition of the vitreous humour vary, however, with age; in the fœtus it is red and contains blood; in old age it sometimes becomes yellow. In the vitreous humour of a blind horse, Lassaigne found a peculiar yellow colouring matter, and 8 per cent. of albumin. (Pelouze et Frémy, *Traité de Chimie générale*, 2<sup>me</sup> édition, vi. 220, 293.)

## F.

**FÆCES.** See EXCREMENTS.

**FAGIN.** A substance found by Buchner and Herberger in beech-nuts, the fruit of *Fagus sylvatica*, but only imperfectly examined. It is said to be a yellow sweetish mass, easily soluble in water and alcohol, sparingly in ether, decomposed by strong acids and by dry distillation, but distilling undecomposed with the vapour of water or alcohol.

**FAGUS.** See BEECH (i. 526).

**FAHL-ERZ.** See TETRAHEDRITE.

**FAHLUNITE.** A variety of hydrous dichroite,  $2M^{10}O.SiO_3 + 2Al^{10}O_3.SiO_3 + 3 aq.$



(p. 310), occurring at Fahlun in Sweden. The crystalline form is the same as that of dichroite, of which indeed it appears to be a pseudomorph. Specific gravity = 2.6 to 2.79. Somewhat harder than apatite. Colour greenish, yellowish, brownish, to black. Lustre feeble, perceptible only on the crystalline faces. Fracture splintery.

*Analyses.*—*a.* by Hisinger (Athandl. i. Fysik, iv. 210).—*b.* Brownish-green; *c.* Black; *d.* Crystallised: by Wachtmeister, Pogg. Ann. xiii. 70).

	SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Mn <sup>2</sup> O	Mn <sup>4</sup> O <sup>3</sup>	Fe <sup>2</sup> O	Fe <sup>3</sup> O	Mg <sup>2</sup> O	CaO	Na <sup>2</sup> O	K <sup>2</sup> O	H <sup>2</sup> O	F
<i>a.</i>	46.79	26.73	. . .	0.43	. . .	5.01	2.97	. . .	. . .	. . .	13.50	. . . = 95.43
<i>b.</i>	43.51	25.81	1.72	. . .	6.35	. . .	6.53	. . .	4.45	0.94	11.66	0.16 = 101.13
<i>c.</i>	44.60	30.10	. . .	2.24	. . .	3.86	6.75	1.35	. . .	1.98	9.35	. . . = 100.23
<i>d.</i>	44.95	30.70	. . .	1.90	. . .	7.22	6.04	0.95	. . .	1.38	8.65	. . . = 101.79

Bonsdorffite from Abo in Finland (p. 321) appears to have the same composition; also peplolite from Sweden and pyrrargyllite from Helsingfors. (Rammelsberg, p. 832.)

**FASSAITE.** A variety of augite from the Fassa valley, Piedmont, having a grass-green or pistachio-green colour, with high lustre.

**FATS.** The term *Fat* was originally applied to all compounds consisting of carbon, hydrogen, and a small quantity of oxygen, which, either at ordinary temperatures form viscid, oily liquids, greasy and leaving a permanent stain on paper, or are converted into such liquids by heat,—which require a strong heat to make them boil, and then distil over in a state of complete, or nearly complete decomposition,—burn with a bright flame, depositing little or no soot,—and are insoluble in water, but soluble in alcohol and in ether.

Fats were divided, according to their various degrees of fusibility, into *liquid fats* or *fatty oils*, *expressed oils*, or *fixed oils*, which, according as they dry up or remain greasy when exposed to the air in thin layers, were subdivided into *drying oils* and *non-drying oils*, and into *solid fats*, such as lard, tallow, wax, spermaceti, cholesterin, &c.

Chevreul, to whose fundamental investigations we are indebted for the greater part of our knowledge of this subject, showed, nearly at the same time with Braconnot, that fats, as they occur in nature, are for the most part mixtures or combinations of different simple fats, *e. g.* of olein, stearin, and margarin, in variable proportions, the consistence and fusibility of the mixture varying accordingly. He showed, moreover, that certain fats (non-saponifiable fats), neither dissolve nor undergo any other change when boiled with aqueous alkalis, whereas most of these bodies form soaps with aqueous alkalis and with certain heavy metallic oxides; that, in this process of saponification, the fats do not combine in their original state with the alkalis, but that they are thereby resolved into two products, viz. first, a fatty acid, which combines with the alkali and forms the soap, and differs in its composition according to the nature of the fat,—and secondly, in most cases, the substance called glycerin, which Scheele obtained by treating fixed oils with lead-oxide and water. He showed that the sum of the weights of these two products, in their utmost state of dryness, exceeds that of the fat employed, and consequently that hydrogen and oxygen from the water must likewise contribute, in equal numbers of atoms, to the formation of the product; whence he concluded that these saponifiable fats are analogous in composition to compound ethers, viz. compounds of various fatty acids with glycerin *minus* a certain quantity of water, just as compound ethers are compounds of alcohol with acids *minus* a certain quantity of water.

In accordance with the investigations of Chevreul, which have since been confirmed and extended, the family of the fats has been broken up, and its members arranged according to their chemical nature, as follows:

1. *Unsaponifiable Fats.*—These substances remain perfectly unaltered even after long boiling with aqueous potash.<sup>2</sup> According to their composition, they belong partly to the hydrocarbons, such as paraffin, partly to the alcohols, as ethal and cholesterin.

2. *Fatty acids or Soap acids.*—Obtained chiefly by the saponification of saponifiable fats. They combine with salifiable bases, without any further addition, and are completely separated therefrom in their original state by stronger acids; hence they properly belong to the class of organic acids, and are in fact included therein. According to their boiling points, they may be divided into *volatile fatty acids*, as butyric, capric acid, &c.; and *fixed fatty acids*, as stearic, palmitic, oleic acid, &c.

3. *Saponifiable Fats.*—These fats do not combine in their entire state with alkalis, but in contact with alkalis and with water are gradually resolved into a fatty acid which unites with the base and forms a soapy salt, and a neutral body, which, in most fats of this kind, is glycerin, but in some, as cerin and spermaceti, is a non-saponifiable fat.

The results obtained by Chevreul have, within these last few years, been confirmed and extended by the researches of Berthelot, who has shown that fats may be artificially produced by the direct union of the fatty acid and glycerin, with elimination of 1, 2, or 3 at. water. The natural fats, stearin, olein, &c. are for the most part of the third class. (See GLYCERIDES.)

**FAUJASITE.** A silicate occurring, together with black augite, in the mandelstein of the Kaiserstuhl in Baden. It crystallises in dimetric octahedrons, in which the angle of the terminal edges is  $111^{\circ} 30'$ , that of the basal edges  $105^{\circ} 30'$ . Hardness = 5. Specific gravity = 1.923. Colourless to brown. Fracture, vitreous and uneven. Gives off water when heated in a tube. Intumesces before the blowpipe, and melts to a white blebby enamel. An analysis by Damour (Ann. Min. [4] xiv. 67) gave 46.12 per cent. silica, 16.81 alumina, 4.79 lime, 5.09 soda, and 27.02 water (= 99.83). Hence the formula  $\left(\frac{1}{2}\text{Ca}^{2+}\text{O}\right) \cdot 3\text{SiO}_2 + 2(\text{Al}^{+3} \cdot 3\text{SiO}_2) + 18 \text{ aq.}$ , which, by substituting  $\text{al} = \frac{1}{2}\text{Al}$ , and, considering part of the hydrogen as basic, may be reduced to the form of a metasilicate  $(\text{M}^{+1}\text{al}^{1/2}\text{H}^+)\text{SiO}_2 + 17 \text{ aq.}$

**FAYALITE.** An iron-chrysolite (*Eisenperidot*),  $\text{Fe}^{+2}\text{SiO}_4$ , occurring in pegmatite on the Mourne mountains, Ireland, also in volcanic rocks at Fayal, one of the Azore islands. It is trimetric, cleavable in two directions at right angles to each other. Hardness = 6.5. Specific gravity = 4.11—4.14; 4.006, according to Delesse. Colour, black, greenish or brownish; sometimes iridescent. Fuses readily to a black magnetic globule, and is easily attacked by acids.

*Analyses.*—1. Thomson (*Outlines of Mineralogy*, i. 461).—2. Delesse (Bull. geol. [2] x. 668).—3. Rammelsberg (*Mineralchemie*, p. 435.)

	$\text{SiO}_2$	$\text{Fe}^{+2}\text{O}$	$\text{Mn}^{+2}\text{O}$	$\text{Al}^{+3}\text{O}_3$	$\text{K}_2\text{O}$	$\text{Mg}^{+2}\text{O}$	$\text{Ca}^{+2}\text{O}$	$\text{Cu}^{+2}\text{O}$	$\text{Fe}^{+3}\text{S}$
1. Slavicarrach, Ireland	29.60	68.73	1.78						= 100.11
2. " "	29.50	63.54	5.07	trace	0.30				= 98.41
3. Fayal	28.27	63.80		3.45		trace	0.45	1.29	3.35 = 100.61

Iron-chrysolite has been observed as a furnace-product near Goslar. A volcanic glass or obsidian analysed by Klaproth (*Beiträge*, v. 222), yielded similar results: 29.50  $\text{SiO}_2$ , 66.00  $\text{Fe}^{+2}\text{O}$ , 4.0  $\text{Al}^{+3}\text{O}_3$ , and 0.25  $\text{K}_2\text{O}$ ; but G. Rose considers it as a slag. (Dana, ii. 185.)

**FAYENCE.** The French name for the glazed earthenware used for common plates, dishes, jugs, and other vessels. (See POTTERY.)

**FEATHER-ALUM.** A name applied to native hydrated sulphate of aluminium  $(\text{Al}^{+3})^{+1}(\text{SO}_4^{+2})^2 + 18\text{H}_2\text{O}$ , and to native iron-alum or halotrichite  $\left(\frac{\text{Fe}}{\text{Al}}\right)^{+2} \cdot 2\text{SO}_4 + 12\text{H}_2\text{O}$ , both of which occur in delicate fibrous crystals or masses. (See SULPHATES.)

**FEATHER-ORE.** This name is applied to the capillary form of native sulphantimonite of lead,  $2\text{Pb}^{+2}\text{S} \cdot \text{Sb}^{+3}\text{S}_2$ ; but as this mineral likewise occurs massive, the name *Heteromorphite* (q. v.) proposed for it by Zincken and Rammelsberg is preferable.

**FEATHERS.** The beard and quill of feathers were found by Scherer to contain:

	C.	H.	N.	O and S.
Beard . . .	52.47 . . .	7.11 . . .	17.68 . . .	22.44 = 99.70
Quill . . .	52.43 . . .	7.21 . . .	17.89 . . .	22.47 = 100.00

whence it appears that the two parts of the feather have essentially the same composition.

The ash of feathers, especially of birds which live on grain, contains a large proportion of silica; the feathers of birds which live on animal food or on berries yield a smaller total amount of ash, and this ash is also less rich in silica, as will be seen from the following table, containing the results obtained by Gorup-Besanez (Ann. Ch. Pharm. lxi. 46; lxvi. 321).

In birds living on:

		Ash.	Silica.	Percentage of silica in the ash.
Seeds . . .	the feathers contain in 100 pts.	4.84	1.98	40
Fish . . .	" "	2.41	0.23	10.5
Flesh . . .	" "	2.16	0.64	27
Insects, Berries	" "	2.62	0.75	27

The feathers of old birds are richer in silica than those of young ones; the wing-feathers contain more silica than those of the tail and breast.

The permanent colours of feathers are due to peculiar pigments which may be

extracted by various solvents. The beautiful play of colours which some feathers exhibit as the light falls upon them at different incidences, arises from a decomposition of light similar to that which is produced by mother-of-pearl and other striated surfaces.

According to Bogdanow (Compt. rend. xlv. 688; xlv. 780) the yellow, green, lilac and red pigments of feathers of constant tint are soluble in alcohol and ether; black feathers contain a pigment (*Zoomelanin*), probably identical with the black pigment of the eye, which is insoluble in alcohol and ether, soluble in ammonia and potash, and slightly in water. Feathers of varying colour yield green and brown pigments, probably identical in composition with the preceding.

Feathers when heated emit a characteristic and unpleasant odour. According to Greville Williams (Chem. Gaz. 1868, p. 309), they yield, when submitted to destructive distillation, considerable quantities of pyrrol, a mixture of volatile bases, and a gas containing sulphur, which quickly decomposes peroxide of lead.

Goose-feathers boiled for a considerable time with dilute sulphuric acid, yield leucine and tyrosine. The beard of feathers heated to 200° C. with water in sealed tubes for several hours dissolves completely, forming a yellowish liquid which smells like burnt feathers, and deposits a flocculent precipitate (Loyer and Keller, Ann. Ch. Pharm. lxxxviii. 332).

Feathers damaged by bending may be completely restored to shape by dipping them for a minute in boiling water, and then in cold water till they are quite cool (Böttger, J. Pharm. [3] xxxiv. 399).

#### **FELDSPAR.** Syn. with FELSPAR.

**FELSITE.** A compact variety of labradorite, which, together with hornblende, forms the greenstone of Siebenlehn in the Erzgebirg. Specific gravity = 2.69. Contains 51.00 per cent.  $\text{SiO}_2$ , 30.50  $\text{Al}_2\text{O}_3$ , 1.75  $\text{Fe}_2\text{O}_3$ , 11.25  $\text{CaO}$ , 4.00  $\text{Na}_2\text{O}$ , 1.25 water (= 99.75). (*Rammelsberg's Mineralchemie*, p. 600.)

#### **FELSOBANYITE.** Syn. with GIBBSITE.

**FELSPAR.** This name\* is applied to a group of minerals which crystallise in the monoclinic and triclinic systems, and may all be represented, either as silicates of alumina united in various proportions with silicates of the alkalis or alkaline earths, or as orthosilicates containing aluminium and an alkali- or alkaline-earth-metal, combined (excepting in the case of anorthite) with excess of silica. On the former mode of representation, they are distinguished from one another by the ratio of the oxygen in the protoxide, the alumina, and the silicic anhydride; in the second, by the proportion of free silicic anhydride associated with the orthosilicate.

The following table shows the composition of the several minerals of the felspar group:

	Oxygen ratio.	
Anorthite	1 : 3 : 4, $\text{Ca}^2\text{O} \cdot \text{Al}^3\text{O}^3 \cdot 2\text{SiO}^2$ or $\text{Ca}(\text{Al}^2)^{\text{III}}\text{SiO}^4$	$= \frac{\text{Si}^{\text{IV}}}{\text{Ca} \cdot \text{Al}^{\text{III}}} \left. \right\} \text{O}^4$
Labradorite	1 : 3 : 6, $\text{M}^2\text{O} \cdot \text{Al}^3\text{O}^3 \cdot 3\text{SiO}^2$ or $2[\text{M}(\text{Al}^2)^{\text{III}}\text{SiO}^4] \cdot \text{SiO}^2$	$= \frac{\text{Si}^{\text{IV}}}{\text{M}^2 \cdot \text{Al}^{\text{III}}} \left. \right\} \text{O}^{10}$
Andesin and Hyalophane	1 : 3 : 8, $\text{M}^2\text{O} \cdot \text{Al}^3\text{O}^3 \cdot 4\text{SiO}^2$ or $\text{M}(\text{Al}^2)^{\text{III}}\text{SiO}^4 \cdot \text{SiO}^2$	$= \frac{\text{Si}^{\text{IV}}}{\text{M} \cdot \text{Al}^{\text{III}}} \left. \right\} \text{O}^8$
Oligoclase	1 : 3 : 9, $2\text{M}^2\text{O} \cdot 2\text{Al}^3\text{O}^3 \cdot 9\text{SiO}^2$ or $4[\text{M}(\text{Al}^2)^{\text{III}}\text{SiO}^4] \cdot 5\text{SiO}^2$	$= \frac{\text{Si}^{\text{IV}}}{\text{M}^2 \cdot \text{Al}^{\text{III}}} \left. \right\} \text{O}^{20}$
Albite and Orthoclase	1 : 3 : 12, $\text{M}^2\text{O} \cdot \text{Al}^3\text{O}^3 \cdot 6\text{SiO}^2$ or $\text{M}(\text{Al}^2)^{\text{III}}\text{SiO}^4 \cdot 2\text{SiO}^2$	$= \frac{\text{Si}^{\text{IV}}}{\text{M} \cdot \text{Al}^{\text{III}}} \left. \right\} \text{O}^8$

If silica be regarded as  $\text{SiO}_2$ , and the small atomic weight of oxygen be used [ $\text{Si} = 21$ ;  $\text{O} = 8$ ], the formulæ become:

Anorthite	$3\text{CaO} \cdot 3\text{Al}^3\text{O}^3 \cdot 4\text{SiO}^2$	Oligoclase	$4\text{MO} \cdot \text{Al}^3\text{O}^3 \cdot 3\text{SiO}^2$
Labradorite	$\text{M}^2\text{O} \cdot \text{Al}^3\text{O}^3 \cdot 2\text{SiO}^2$	Albite and Orthoclase	$2\text{MO} \cdot \text{Al}^3\text{O}^3 \cdot 4\text{SiO}^2$
Andesin and Hyalophane	$3\text{M}^2\text{O} \cdot 3\text{Al}^3\text{O}^3 \cdot 8\text{SiO}^2$		

\* It is sometimes written "Feldspar," in imitation of the German *Feldspath*, derived from *Feld* a field; but "Felspar," signifying a spar found on a rock or *fel*, is the more correct spelling.



We shall here describe only the two minerals to which the name feldspar is more especially applied, viz. *Orthoclase*, or *Potash-feldspar*, and *Albite*, or *Soda-feldspar*. The rest have been or will be described in separate articles.

The two species of feldspar just named are distinguished, partly by their crystalline forms, partly by their chemical composition, orthoclase being monoclinic, and containing, for the most part, more potash than soda, while albite is triclinic, and contains more soda than potash. In one or two varieties of orthoclase (known to be such by their cleavage), the proportion of soda exceeds that of potash, as in glassy feldspar from Langenberg (Analysis, 16, p. 620), and in loxoclase; but in triclinic feldspar, the soda invariably predominates, the proportion of potash never amounting to one-third that of the soda; so that it may be stated as generally true that excess of potash determines the monoclinic and excess of soda the triclinic form. The alkali present in the smaller proportion appears, however, to have some influence on the crystalline form: for, according to observations of Breithaupt and of Naumann, it appears that in some varieties of potash-feldspar, the inclinations of the axes are somewhat different from that which exists in normal orthoclase, so that the forms pass into the clinclinic and even into the triclinic system.

Orthoclase and albite may also be distinguished to a certain extent by their density, that of albite being for the most part somewhat above that of orthoclase; but this criterion is not very decided, inasmuch as the density of a feldspar may be increased by an augmented proportion of lime.

**Orthoclase.** *Common or Potash Feldspar. Ice-spar. Felsite. Adularia. Moonstone. Murchisonite. Leelite. Amauite. Amazon-stone. Sanidin. Napoleonite. Necronite. Pegmatolite. Mikroklin (Breithaupt). Valencianite (Breithaupt). Erythrite and Perthite of Thomson.*

*Monoclinia.*—Some of the most frequently occurring forms are shown in *figs. 471—476*. Ratio of axes,  $a : b : c = 1.519 : 1 : 0.844$ ;  $\infty P : \infty P$  in the orthodiagonal prin-

Fig. 471.

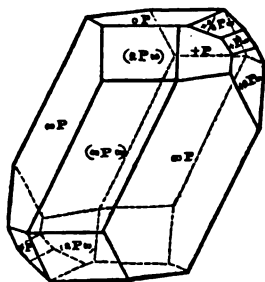


Fig. 472.

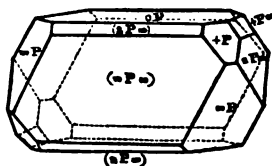


Fig. 473.

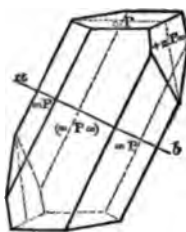


Fig. 474.

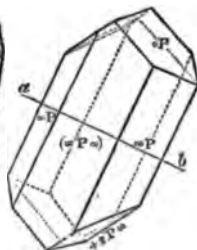


Fig. 475.

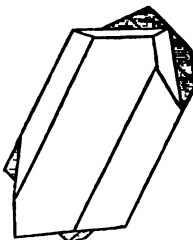
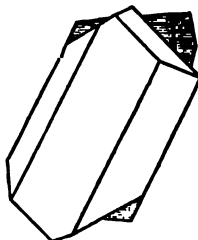


Fig. 476.



cipal section  $= 61^\circ 11'$ ;  $\infty P : \infty P = 67^\circ 44'$ . The crystals are often prismatically elongated in the direction of the principal axis (*figs. 471, 473*) or in that of the clinodiagonal (*fig. 472*); frequently also they assume the tabular form from predominance of the face  $\{ \infty P \infty \}$ . Twin-crystals are of frequent occurrence, like those in *figs. 475, 476*, for the description of which see CRYSTALLOGRAPHY (p. 163); more rarely the combination-face is parallel to the face of a clinodiagonal dome  $\{ 2P \infty \}$ . Cleavage

perfect parallel to  $oP$ ; less perfect parallel to  $[\infty P\infty]$ . Often massive, cleavable, or granular, sometimes coarsely lamellar.

Hardness = 6. Specific gravity = 2.4–2.62. Lustre vitreous, sometimes inclining to pearly on the surface of perfect cleavage. Colour white, grey, reddish-white, flesh-red, greenish-white, green. Streak uncoloured. Transparent to translucent. Fracture conchoidal to uneven.

Before the blowpipe it melts with difficulty to a semi-transparent blebby glass (at the heat of the porcelain furnace, to a greyish white frothy glass). According to Turner, many altered felspars give a slight indication of the presence of boric acid. It is not attacked by acids.

*Analyses*.—1. Valentine Rose (Scherer's J. viii. 244).—2. Delesse (Bull. geol. [2] x. 568).—3. Gmelin (Pogg. Ann. lxxxi. 313).—4. Abich (*ibid.* li. 528).—5. Brogniart and Malaguti (Ann. Min. [4] ii. 465).—6. Plattner (Pogg. Ann. xvi. 299).—7. Evreinoff (*ibid.* lxvii. 421).—8. T. S. Hunt (Phil. Mag. [4] i. 322).—9. 10. Smith and Brush (Sill. Am. J. [2] xvi. 42).—11. Berthier (Rammelsberg's Mineralchemie, p. 626).—12. Rothe (*ibid.*).—13. Abich (*ibid.*).—14. G. Rose (*ibid.*).—15. Schnabel (*ibid.*).

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	Loss by ignition
1. Common felspar, Lomnitz . . .	66.75	17.50	1.75	1.25	. .	12.00	. .	98.25
2. Common felspar, Chamounix . .	66.48	19.06	trace	0.63	. .	10.32	2.30	98.59
3. Common felspar, greenish, Laurvig .	65.90	19.46	0.44	0.28	. .	6.55	6.14	0.12 = 98.49
4. Adularia, St. Gothard . . .	65.69	17.57	. .	1.34	. .	13.59	1.01	. . = 100.00
5. Moonstone, Ceylon . . .	64.00	19.43	. .	0.42	0.20	14.81	. .	1.14 = 100.00
6. Valencianite . . .	66.82	17.58	0.09	. .	. .	14.80	. .	99.29
7. Microcline . . .	65.76	18.31	trace	1.20	. .	14.06	. .	99.33
8. Perthite . . .	66.44	18.35	1.00	0.67	0.24	6.37	5.56	0.40 = 99.03
9. Chesterite . . .	64.76	17.60	0.50	0.65	0.30	14.18	1.75	0.65 = 100.39
10. Loxoclase . . .	65.40	19.48	1.25	2.25	0.20	2.76	7.23	0.76 = 99.34
11. Glassy felspar, Drachenfels . .	66.60	18.50	0.60	1.00	. .	8.00	4.00	. . = 98.70
12. Glassy felspar, Rockeskyll, Eifel .	65.84	17.61	0.74	0.18	0.06	14.39	1.18	. . = 100.00
13. Glassy felspar, Epomeo, Ischia . .	66.73	17.56	0.81	1.23	1.20	8.27	4.10	. . = 99.90
14. Glassy felspar, Vesuvius . . .	65.52	19.15	. .	0.60	. .	14.74	. .	100.81
15. Glassy felspar, Langenberg, Siebengebirg . . .	66.33	19.02	0.52	0.76	. .	6.02	7.32	. . = 99.97

The formula  $K^2O \cdot Al^2O_3 \cdot 6SiO_2$  requires 64.8 SiO<sub>2</sub>, 18.4 Al<sub>2</sub>O<sub>3</sub>, 16.8 K<sub>2</sub>O = 100.

Soda, as already observed, generally replaces part of the potash and sometimes even predominates, as in loxoclase. Lime and magnesia are almost always present to a small amount, some glassy felspars containing as much as 2½ to 2¾ per cent. of lime. Felspar also contains a small quantity of phosphoric acid. (Fownes, Ann. Ch. Pharm. lx. 190.—Sullivan, Phil. Mag. [3] xxvii. 161.)

The different varieties of felspar are distinguished by their colour, lustre, and transparency. The common subtranslucent variety, or orthoclase, is the ordinary constituent of granite: it occurs in fine crystals at Baveno on the Lago Maggiore, Lomnitz in Silesia, Carlsbad and Einbogen in Bohemia, Arendal in Norway, the Land's End, the Mourne Mountains in Ireland, Alabashka, and other places in the Ural, near Rio Janeiro, at Rossie in St. Lawrence County, New York, and other localities. *Loxoclase* found at Hammond, in St. Lawrence County, N. Y., is distinguished by more distinct cleavage parallel to the basal and clinodiagonal sections. Specific gravity = 2.6–2.62 (Plattner.) *Neeromite* is a variety which gives off a fetid odour when struck.—*Chesterite* is from Chester County, Pennsylvania.—*Adularia* is a transparent or translucent variety, found in granitic rocks. Large crystals of it are found on the St. Gothard.—*Valencianite* is a variety of adularia from the Valenciana mine, in Mexico.—*Moonstone*, from Ceylon, is also a variety of adularia, exhibiting pearly reflections when polished.—*Sunstone* is a similar variety, containing minute scales of oxide of iron.—*Aventurin felspar* is less pellucid, and has yellow and reddish internal reflections.—The *Murchisonite* of Levy is a flesh-red variety of felspar (specific gravity = 2.51) occurring in rolled pebbles at Heavitree, near Exeter.—*Amazon-stone* is a verdigris-green variety, coloured by copper, from Lake Ilmen.—*Leelite* or *Helleflinta*, from Gryphyttan, in Sweden, has a waxy lustre, and deep flesh-red colour.—*Variolite* is a dark green variety, containing lighter globular particles, from the river Drac, in France.—The *Microclin* of Breithaupt, is a variety of felspar from Arendal; the *Erythrite* of Thomson is a flesh-coloured felspar, containing 3 per cent. magnesia, found in amygdaloid. Specific gravity = 2.541.—The *Perthite* of Thomson, is from Perth in Upper Canada.

All the varieties of felspar above mentioned occur in rocks of the older formations; *glassy felspar*, also called *Saundin* (from *savus*, a board, the crystals being tabular), is found in trachytic and volcanic rocks of recent origin; it has a perfect vitreous lustre, and is traversed by numerous cracks. A variety called *Ice-spar* is found in the Vesuvian lavas; the *Rhyacolite* of G. Rose is also a glassy felspar from Vesuvius.

According to Bischof, the mode of occurrence of felspar, and the minerals with which it is associated, are, in most cases, such as prove it to have been formed by reactions

that have taken place in the wet way, although the possibility of its formation by fusion is established by its occurrence in violet-coloured crystals on the inner walls of a smelting furnace at Sangerhausen. (*Chem. and Phys. Geology*, by Gustav Bischof, Eng. edit. ii. 162, *et. seq.*)

**Alterations of Felspar.**—Felspar is altered by the action of water containing carbonic acid (Forchhammer), or rendered acid by the decomposition of pyrites (Mitacherlich), or containing alkaline and other ingredients in solution, the change consisting in the abstraction of the alkali and a portion of the silica, and the assumption of water. The ultimate products of this alteration are hydrated silicates of aluminium, viz. *kaolin* and its varieties, *pholerite*, *halloysite*, *samoite*, and *bole*, and the several kinds of clay. The following are analyses of partially decomposed felspars.

*a.* Orthoclase from the porphyry of the Auerberg, near Stolberg, in the Harz; white, rather soft (Rammelsberg, *Mineralchemie*, p. 629).—*b.* Decomposed orthoclase from the granite of Karlsbad.—*c.* The same from the syenite of Geising, near Altenberg, in the Erzgebirg.—*d.* The same from the red porphyry of Ilmenau, in the Thüringerwald (Crasso, *loc. cit.*):

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Mn <sub>2</sub> O	Ca <sub>2</sub> O	Mg <sub>2</sub> O	K <sub>2</sub> O	Na <sub>2</sub> O	H <sub>2</sub> O	Ca <sub>2</sub> CO <sub>3</sub>
<i>a.</i> 66.26	16.98	0.31	. .	0.43	0.11	14.42	0.20	1.29	. . = 100
<i>b.</i> 54.17	29.93	1.22	. .	0.59	0.46	4.67	0.41	8.51	. . = 99.96
<i>c.</i> 70.79	17.09	1.15	. .	0.35	0.65	5.86	0.38	3.67	. . = 99.94
<i>d.</i> 23.17	7.30	12.53	0.17	. .	0.61	2.12	0.21	. .	49.46 = 95.57

In *a* the alteration is rather mechanical than chemical. The deficiency in *d* is probably due to loss of water in the analysis.

Felspar is also gradually converted by loss of silica and alkali, into mica. This transformation, first observed by G. Rose in the felspar crystals of Lomnitz and Hirschberg in Silesia, has lately been more exactly investigated by v. Rath (Pogg. Ann. xcvi. 280). In the three following analyses, *a* is the flesh-red orthoclase in the interior of the mass, of specific gravity 2.544, and yielding only traces of water when heated. The zone of weathered mineral *b*, immediately surrounding this is greenish-white, granular, friable, of rough, uneven fracture, and filled throughout its mass with specks of silvery lustre; its specific gravity is 2.616. The external layer *c* consists of mica in greenish scales, which turn brown when heated; their specific gravity is 2.867. For analysis they were separated from intermixed quartz-granules.

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Ca <sub>2</sub> O	Mg <sub>2</sub> O	K <sub>2</sub> O	Na <sub>2</sub> O	Loss by ignition.
<i>a.</i> 66.66	18.86	0.46	0.36	0.21	11.12	3.01	0.50 = 101.18
<i>b.</i> 65.48	20.34	1.32	0.54	0.30	9.21	2.08	1.34 = 100.61
<i>c.</i> 49.04	29.01	5.56	0.17	0.75	11.19	0.50	4.65 = 100.87

The Orthoclase, in changing into mica, parts with about half its alkali and  $\frac{1}{2}$  of its silica. (*Rammelsberg's Mineralchemie*, p. 630.)

**Albite.** Soda-felspar. *Cleavandite*. *Periclin*. *Tetartine*. *Kieselspath*.

Triclinic, an ordinary combination being  $\infty P$ ,  $\infty \bar{P}$ ,  $\infty P.P$ ,  $\bar{P} \infty$  (fig. 477). Cleavage very perfect parallel to  $\infty P$ ; less distinct parallel to  $\infty \bar{P}$ ; imperfect parallel to  $P$ . Twin crystals are frequent, generally having the face of combination parallel to  $\infty \bar{P}$  (fig. 478) see p. 266; indeed the tendency of this mineral to form twins is so

Fig. 477.

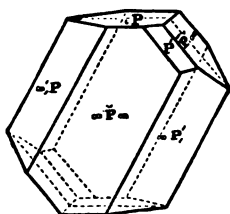
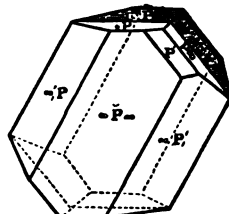


Fig. 478.



great, that even crystals and crystalline fragments of apparently simple structure are generally found to consist of a large number of lamellar twins, producing on certain fractured surfaces striations which are characteristic of albite. The mineral likewise occurs lamellar and granular, sometimes almost impalpable.

Hardness = 6–6.5; in some granular varieties = 7. Specific gravity = 2.59–2.65.



Lustre, vitreous; on the cleavage-faces, pearly. Colourless, white of various shades, light red, yellow, green, and grey. Streak uncoloured. Transparent to subtranslucent, Fracture uneven. Brittle.—Before the blowpipe, it behaves very much like orthoclase, but melts somewhat more easily, and colours the flame distinctly yellow.

*Analyses*.—1. G. Rose (Pogg. Ann. lxxiii. 173).—2. Thaulow (*ibid.* xlii. 571).—3. Abich (Berg. u. hüttenm. Zeitung, 1842, No. 19).—4. Stromeyer (*Untersuchungen*, p. 300).—5. Abich (*loc. cit.*).—6. Hunt (Phil. Mag. [4] i. 322).—7. Rammelsberg (*Mineralchemie*, p. 620).

	SiO <sub>2</sub>	Al <sup>4</sup> O <sub>3</sub>	Fe <sup>4</sup> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	Mn <sub>2</sub> O
1. <i>Crystallised</i> , Arendal	68.46	19.30	0.28	0.68	. . .	. . .	9.12	. . . = 97.84
2. " St. Gothard	69.00	19.43	. . .	0.20	. . .	. . .	11.47	. . . = 100.10
3. " Minsk	68.45	18.71	0.27	0.50	0.18	0.65	11.24	trace = 100.00
4. <i>Massive</i> , Chesterfield	70.68	19.80	0.11	0.24	. . .	. . .	9.06	. . . = 99.89
5. <i>Periclin</i> , Pantellaria	68.23	18.30	1.01	1.26	0.51	2.53	7.99	. . . = 99.83
							Ign.	
6. <i>Peristerite</i> , Perth, } Lower Canada }	66.80	21.80	0.30	2.52	0.20	0.58	7.00	0.6 = 99.80
7. <i>Hypoclerite</i> , Arendal	67.62	16.59	2.30	0.85	1.46	0.51	10.24	. . . = 99.57

The formula  $\text{Na}_2\text{O} \cdot \text{Al}^4\text{O}_3 \cdot 6\text{SiO}_2$  requires 68.7 SiO<sub>2</sub>, 19.5 Al<sup>4</sup>O<sub>3</sub>, 11.8 Na<sub>2</sub>O = 100.

*Hypoclerite*, which has a specific gravity of 2.6–2.66, and is softer than albite, is, according to Rammelsberg, a mixture of albite with 5 per cent. augite.—A white massive feldspar from the St. Gothard, containing nearly equal quantities of potash and soda (67.39 SiO<sub>2</sub>, 19.24 Al<sup>4</sup>O<sub>3</sub>, 0.31 CaO, 0.61 MgO, 6.77 K<sub>2</sub>O, and 6.23 Na<sub>2</sub>O), appears to be a mixture of albite and orthoclase.

Albite often replaces orthoclase as a constituent of granite; in other instances it is associated with orthoclase, as in Pompey's pillar, and may then be distinguished by its superior whiteness. The albite granites are often repositories of several of the granite minerals, *e. g.* tourmalin, beryl, and allanite. Albite is associated with pearlspar in the Tyrol, where it occurs in large transparent crystals; with epidote and garnet at Arendal; with eudialyte and hornblende in Greenland. It is frequently one of the constituents of syenite and greenstone. (Dana, ii. 240.)

Soda-feldspars yield more rapidly than potash-feldspars to the decomposing action of water containing carbonic acid; and, accordingly, Mr. Sterry Hunt finds in the more recent crystalline or metamorphic rocks of Canada "a less development of soda-feldspar, while orthoclase and mica, chlorite and epidote, and silicates of alumina, like chiastolite, kyanite, and staurolite (which contain but little or no alkali, and are rare in the older rocks) become abundant." He conceives the carbonate of sodium resulting from the decomposition of the albite and similar minerals of the older rocks, to have reacted with the chloride of calcium which existed in large proportion in the paleozoic ocean, thus giving rise to deposits of carbonate of calcium, and to the chloride of sodium which sea water now contains. (Proc. Geol. Soc. Lond. Jan. 5, 1859.)

*Green Feldspar of Bodenmais*.—This mineral which occurs associated with magnetic pyrites, quartz, &c., exhibits on the cleavage-faces the striation of the triclinic feldspars, and has a specific gravity = 2.546–2.549 (Kerndt), 2.604 (Potyka). Heated in splinters before the blowpipe, it melts to a blebby glass, and colours the flame reddish-yellow. Contains, according to Potyka (Pogg. Ann. cviii. 363):

SiO <sub>2</sub>	Al <sup>4</sup> O <sub>3</sub>	Fe <sup>2</sup> O	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O
63.12	19.78	1.51	0.65	0.13	12.57	2.11 = 99.87;

whence Rammelsberg (*Mineralchemie*, p. 616) deduces the formula  $\frac{\text{K}_2\text{O}}{\text{Na}_2\text{O}} \left\{ 2\text{SiO}_2 + \text{Al}^4\text{O}_3 \cdot 3\text{SiO}_2 \right\}$ —which is of the form  $\text{M}^2\text{O} \cdot \text{Al}^4\text{O}_3 \cdot 5\text{SiO}_2$ , or  $2[\text{M}(\text{Al}^4\text{O}_3 \cdot \text{SiO}_2) \cdot 3\text{SiO}_2]$ . The mineral is perhaps a new member of the feldspar group (p. 618), intermediate in composition between oligoclase and orthoclase, between which it also stands with regard to its density.

**FELSPATHIC ROCKS.** Feldspar—chiefly orthoclase and its varieties—enters into the composition of a great number of rocks. *Granite* consists of feldspar (generally orthoclase), quartz, and mica, crystallised promiscuously together. *Pegmatite* is graphic granite. *Gneiss* has the same composition as granite, but exhibits traces of lamination. *Mica slate* is similar, but with a distinctly foliated structure. *Beresite* is a fine-grained granite, containing pyrites, from the neighbourhood of Beresof in the Ural. *Syenite* resembles granite, but contains hornblende in place of mica. *Protophine* is a tale granite.

*Dolerine* is a gneissoid rock in the Alps, consisting of feldspar and talc. *Granulite*,

*Eurite*, or *Leptynite* is a granular compound of felspar and quartz, sometimes with garnet. *Hornfels* and *Cornubianite* also consist of quartz and felspar. *Pyroxenite* consists of felspar and lamellar pyroxene. *Pyromeride* is a granitoid rock, containing thickly disseminated spherules of a felspathic rock, mixed with quartz. *Miascite* is a granular slaty rock, consisting of orthoclase, mica, and *elsolite*, sometimes with quartz, albite, and hornblende.

*Porphyry* consists of a compact felspathic base (*cornite* or *porphyrite*), intermixed with crystals of felspar (orthoclase, oligoclase, or labradorite). See PORPHYRY.

*Clinkstone* or *Phonolite* is a compact felspathic rock, of greyish colour and smooth fracture, clinking under the hammer somewhat like a metallic ore. *Trachyte* is similar in colour and constitution, but has a rough surface of fracture. *Domite* is a greyish earthy variety from the Puy-de-Dome.

*Pumice* is a porous felspathic scoria from volcanoes.

*Trap* or *Greenstone* is a dark-heavy blackish-green, green, or brownish rock, consisting of felspar and hornblende. When albite replaces orthoclase, the rock is called *diorite*. *Basalt* (i. 618) is a similar rock, consisting of felspar (generally labradorite) with augite, olivine, magnetic iron ore, and a zeolite. *Dolerite* (p. 343), is similar to basalt, but does not contain olivine, or generally zeolites. *Anamesite* is a fine-grained rock, similar to basalt, in which labradorite predominates. *Wacke* is an earthy variety or a rock consisting of basaltic earth or sand.

*Petrosilex*, or *Adinole*, is a compact impure felspar, like the base of porphyries. *Obsidian* or volcanic glass, is sometimes impure glassy felspar, sometimes a mixture of felspar and augite, with chrysolite and much iron, &c., according to the nature of the lava from which it is formed. (See OBSIDIAN.)

*Pitchstone* and *Pearlstone* are felspathic minerals, containing excess of silica, like the spherules of pyromeride, porphyry, &c. *Baulite* or *Krabite* (i. 622) appears to be a siliceous felspathic mineral related to these concretions: it forms the basis of the trachyte, obsidian, and pitchstone of Iceland. (Dana, ii. 246.)

**FENNEL, OIL OF.** The essential oil of common fennel (*Faniculum vulgare* or *Anethum faniculum*) is identical with oil of anise (i. 297). The oil of bitter fennel (? of *Phellandrium aquaticum*) is a mixture of two volatile oils differing in boiling point (i. 299).

**FERGUSONITE.** A rare mineral from Kikertaursak in Greenland, discovered by Hartwall (K. Vet. Acad. Förh. 1828, p. 167), further examined by Weber. It crystallises in quadratic sphenoids (p. 136) with imperfect cleavage, parallel to the pyramid of the primary form. Hardness = 5.5—6. Spec. grav. = 5.838 (Allan), 5.800 (Turner). Lustre, dull externally, brilliantly vitreous and submetallic on the fractured surface. Colour brownish-black; in thin scales, pale liver-brown. Streak pale brown. Subtranslucent to opaque. Fracture imperfect conchoidal. Infusible before the blowpipe. With fluxes it melts with difficulty, forming glasses which appear yellow while hot. The glass formed with phosphorus-salt appears reddish in the reducing flame; when saturated with soda it yields globules of tin.

The mineral is a hyponiobate (originally regarded as a tantalate) of yttrium and cerium, containing also zirconic and stannic acids, as shown by the following analyses, *a* by Hartwall, *b* by Weber:

	Nb <sup>2</sup> O <sup>3</sup>	SnO <sup>2</sup>	ZrO <sup>2</sup>	Y <sup>2</sup> O	Ce <sup>2</sup> O	U <sup>2</sup> O	Fe <sup>2</sup> O
<i>a.</i>	47.75	1.00	3.02	41.91	4.68	0.95	0.31 = 99.62
<i>b.</i>	48.84	0.35	6.93	38.61	3.05	0.35	1.33 = 99.46

From Weber's analysis we may deduce the formula  $M^2O(ZrO^2; SnO^2) + 2(M^2O. NbO^2) = M^2(Zr; Sn)O^2.4MnBO^2$ . (Rammelsberg's Mineralchemie, p. 401.)

**FERMENTATION and PUTREFACTION.** (Berzelius, Berz. Jahresber. xx. 464. — Liebig, Handw. d. Chem. iii. 217. — Schwann, Pogg. Ann. xli. 184. — Helmholtz, J. pr. Chem. xxxi. 429. — Döpping and Struve, *ibid.* xli. 255. — Blondesin, J. Pharm. [3] xii. 244, 333. — C. Schmidt, Ann. Ch. Pharm. lxi. 128; cxix. 126. — Pasteur, *Vinous Fermentation*, Ann. Ch. Phys. [3] lviii. 323; *Lactous Fermentation*, *ibid.* lii. 404; Jahresber. d. Chem. 1857, p. 510; 1859, p. 553; *Mucous Fermentation*, Bull. Soc. Chim. 1861, p. 30; *Spontaneous Decomposition*, Ann. Ch. Phys. [3] lxiii. 5. — Gm. vii. 96; xv. 265.)

Certain organic compounds, when exposed to the action of air, water, and a certain temperature, undergo decomposition, consisting either in a slow combustion or oxidation by the surrounding air, or in a new arrangement of the elements of the compound in different proportions (often with assimilation of the elements of water), and the consequent formation of new products. The former process, that of slow combustion, is called *Eremacausis* or *Decay*, and has been already considered (p. 497); the latter is



called *Putrefaction* or *Fermentation*,—*putrefaction*, when it is accompanied by an offensive odour, *fermentation* when no such odour is evolved, and especially if the process results in the formation of useful products; thus the decomposition of a dead body or of a quantity of blood or urine, is putrefaction; that of grape-juice or malt-wort, which yields alcohol, is fermentation.

In the processes of fermentation and putrefaction, organic compounds of a higher order are resolved, sometimes into lower organic compounds, sometimes into inorganic compounds, as carbonic acid, water, ammonia, or sulphuretted hydrogen, sometimes into simple substances, as hydrogen and nitrogen gases. In many fermentations, none of the above-mentioned gases are evolved; in fact, they go on without any evolution of gas. The affinities which tend towards the formation of organic compounds of a lower order, or of inorganic products, are doubtless stronger than those by which the original substance is held together; and this circumstance is probably connected with the evolution of heat which accompanies fermentation, and may be partly the cause of the spontaneous combustion of organic bodies.

Fermenting and putrefying substances generally have a tendency to abstract oxygen from the air and other bodies. Hence, when fermentation takes place with free access of air, it is accompanied by *eremacausis* on the surface of the organic substance.—Putrefying substances reduce sulphide of iron from ferrous sulphate. The warm fermentation of indigo is likewise a process of the same nature.

The substances most disposed to putrefaction are numerous compounds rich in nitrogen, viz. the albuminous or protein substances, such as albumin, fibrin, casein, emulsin, legumin, gliadin, gluten, &c., and gelatinous substances, such as membranes consisting of gelatin and other tissues, glue, chondrin, &c. On the other hand, there are other compounds rich in nitrogen, such as uric acid, the alkaloids, indigo, &c., which, of themselves, at least, are not capable of putrefying, and even some substances belonging to the class of protein-compounds, but of a coherent nature, such as hair, horn, and hard-boiled albumin, are susceptible only of a slow decay. The former compounds, on the contrary, require only the presence of water and the access of air at the commencement, to bring them into a state of decomposition, which, on account of the offensive odour which accompanies it, is especially denoted by the term *putrefaction*. Since animals are mainly composed of these substances, they are especially liable to this putrid decomposition; but many seeds of plants, mosses, &c., which are likewise rich in protein-compounds, are also liable to pass into the state of stinking putrefaction. The bad smell which accompanies putrefaction, proceeds partly from inorganic compounds, such as sulphuretted hydrogen and ammonia, partly from newly formed volatile organic compounds, the nature of which is not exactly known.

Of other organic compounds, there are but few which are brought into a state of fermentation or putrefaction by contact with air and water, so long as gelatin and albuminous compounds are excluded. Urea dissolved in a very large quantity of water is very slowly resolved into ammonia and carbonic acid; dilute aqueous solutions of many vegetable acids, and more especially of their ammoniacal salts, also of sugar, gum, and starch, are decomposed with formation of mould.

But many substances incapable of fermenting *per se*, undergo that change when in contact with gelatinous or albuminous compounds; and those which are capable of fermenting alone ferment more quickly, or with formation of different products, when they are brought in contact with these compounds. Many compounds, however—those, namely, which consist wholly of carbon and hydrogen—are incapable of fermenting even under these circumstances. As gelatinous and albuminous compounds excite fermentation in other substances, they are called *Ferments*, and the compounds which are brought into the fermenting state by contact with them are called *Fermentable Substances*.

Albuminous and gelatinous compounds sometimes excite fermentation in other substances, even when they are in the fresh state, as they exist in plants and animals;—sometimes, on the contrary, they must be exposed to the air, so as to bring them into a state of incipient putrefaction, before they will act as ferments upon other bodies; and, in this case, it is often found that they will bring another substance into different states of fermentation, according to the particular stage of decomposition which they have themselves attained.

The aqueous solution of salicin or amygdalin would probably remain unaltered for a long time, if left to itself; but the emulsion of almonds (*Synaptase*) added in its unaltered state, just as it exists in recently prepared sweet almond-milk, decomposes salicin into glucose and saligenin, and amygdalin into glucose, bitter-almond oil, and hydrocyanic acid.—In black mustard, the addition of water induces the formation of volatile oil of mustard, in consequence of the action of the emulsin-like substance contained in it on the myronic acid which it also contains.



Fixed oils appear to pass into a state of rancid putrefaction only when an albuminous compound is mixed with them.

Starch boiled to a paste with water, and then left to itself in a close vessel for some weeks, is in great part converted into glucose, with evolution of carbonic anhydride and hydrogen; but in contact with gluten at 60° C. the starch of the paste is converted into glucose in eight hours; lastly, if the gluten has previously passed into that peculiar condition in which it exists as germinated gluten or *diastase* in malt, it effects this conversion of the starch at 60° C. in less than an hour.

A dilute aqueous solution of glucose or cane-sugar, which remains unaltered when alone, or only forms a little mould and mucus after a long time, may be brought, according to the nature of the ferment and its stage of decomposition, and according to the temperature and dilution of the solution, into three different states of fermentation; whereby it is converted either into lactic and then into butyric acid (*Lactous* and *Butyrous Fermentation*),—or into a mucous substance allied to gum, and generally at the same time into mannite (*Mucous Fermentation*),—or resolved into carbonic anhydride and alcohol, together with small quantities of succinic acid and glycerin. (*Vinous Fermentation*.)

The putrefaction of albuminous and gelatinous substances is prevented by a variety of circumstances, which likewise interrupt its further progress when it has already begun. The same circumstances likewise prevent or interrupt the fermentation of any fermentable materials that may be mixed with the ferment. Among these circumstances are the following:

1. *Exclusion of the air*.—Keeping the substances in a vacuum, in water free from air, in hydrogen, nitrogen, carbonic anhydride, and other gases which cannot furnish oxygen to the nitrogenous substances, or covering them with oil, butter, tallow, wax, or resin.—Wood immersed in the depths of lakes and peat-mosses, where no oxygen absorbed from the air can reach it, because it is intercepted on the way by organic substances diffused through the water, remains unaltered for thousands of years.—This exclusion of air may prevent incipient putrefaction, but does not usually interrupt the progress of that which has already begun. According to Schwann and others (p. 626), exclusion of air acts, not by intercepting oxygen, but by preventing the admission of the germs of microscopic plants and animals diffused through the air.

2. *Dryness*.—Perfect dryness prevents every kind of fermentation or putrefaction, and seldom allows even of slow combustion: *e. g.* the preservation of wood for three thousand years in Egyptian tombs, where it has been exposed only to the action of tolerably dry air.

3. *Freezing temperature*.—Water in the solid state is quite inactive, and does not allow fermentation or putrefaction to go on; but even at a few degrees above 0° C., certain kinds of fermentation do not take place, and others are very slowly produced. All kinds of fermentation and putrefaction appear to take place most readily between 20° and 40° C.—Mammoths have remained undecomposed for thousands of years in the ice of Siberia.

4. *Boiling heat* prevents incipient fermentation, and completely stops that which has already begun, either because all ferments are altered by it, in a similar manner to albumin, which, when boiled hard, is scarcely susceptible of putrefaction; or because it kills the microscopic plants and animals and their germs; or from both causes together. Fermentation prevented or interrupted by a boiling heat, does not recommence after cooling, if the air be perfectly excluded, because either oxygen or living germs are required to produce new ferment.

On this principle is founded Appert's process, by which easily decomposable articles of food and drink, such as meat, fish, vegetables, milk, &c., may be preserved for years,—*viz.* by packing them in air-tight bottles or soldered tin-cases, heating the vessels for several hours in boiling water and keeping them carefully closed. To explain this action, we may either suppose, with Liebig, that the small quantity of oxygen contained in the enclosed air is taken up by the organic matter, without being able to produce ferment at that temperature, or, with Schwann, that the microscopic organisms are killed by the heat.

If the air be admitted, the boiled substance passes again, after a while, into the fermenting state.—If, however, grape-juice, milk, meat, &c., be exposed once a day to a boiling heat, without being protected from the air, and the small quantity of reproduced ferment thereby rendered inactive, before it has time to act upon the rest of the mass, fermentation may be prevented for any length of time.

5. *Antiputrescent or Antiseptic Substances*.—By the addition of various substances, organic and inorganic, fermentable bodies are deprived of their tendency to fermentation, and fermentation already commenced is interrupted.

These antiputrescent bodies probably act in various ways:

a. They abstract water from the fermentable substance.

*b.* They form with it a compound less liable to fermentation.

*c.* They decompose the ferment in such a manner as to deprive it of its tendency to fermentation.

*d.* They take from the surrounding air, and also from the ferment already oxidised by it, the oxygen required for fermentation.

*e.* They probably kill the fungi and infusoria and their germs.

The action mentioned in *a* is probably exerted by powdered sugar in contact with meat and fresh cut-up vegetables; the solution of sugar thereby formed is too strong to ferment.—*a* and *b* together: The stronger mineral acids, such as sulphuric acid, alum, ferric sulphate, mercuric chloride, and other salts of heavy metals; also tannin and creosote.—*c.* Chlorine, pernitric oxide, and chromate of potassium.—*d.* Probably sulphurous acid.—*e.* Arsenious acid, mercuric chloride, and several other of the substances above mentioned. Arsenious acid and mercuric chloride kill fungi and infusoria; *aur vomica* only the latter.

*Theories of Fermentation.*—Respecting the exciting cause of fermentation and putrefaction two opposite views are entertained; the one attributing these changes entirely to the action of chemical and physical forces, the other supposing that they cannot take place without the intervention of living organisms, viz. fungi and infusoria.

In inquiring into the exciting cause of these phenomena, there are two essential conditions to be taken into account.

1. *The presence of a nitrogenous body.*—It is only nitrogenous compounds, such as albumin, gelatin, &c., that are subject to spontaneous fermentation or putrefaction. Organic compounds containing only carbon, hydrogen, and oxygen, do not ferment except when in contact with nitrogenous bodies.

2. *Contact with the air.*—This condition is necessary for the commencement of the process, but not for its continuance. A body once brought into a state of fermentation or putrefaction by contact with the air, continues to ferment or putrefy when afterwards excluded from the air, provided there is a sufficient amount of nitrogenous matter present. The juice of the grape does not ferment while enclosed in the sound skin of the fruit; but the slightest puncture which admits the air, causes fermentation to begin, and the process will then go on even in a vessel filled with carbonic anhydride or hydrogen, and hermetically sealed.

From these circumstances, Berzelius and Liebig conclude that the exciting cause of fermentation and putrefaction is to be found in the oxygen of the air. The nitrogenous matter, by contact with atmospheric oxygen, undergoes a change of composition, by which the equilibrium of the attractive forces, which hold its particles together is disturbed, and new compounds are formed; this alteration of arrangement in the atoms of the elements, produces a motion in the compound molecule of the nitrogenous body, which motion is transferred from one molecule to the next; and in this manner the decomposition is propagated throughout the whole of the nitrogenous body.—Further, when a nitrogenous substance in this state of decomposition comes in contact with another substance, such as sugar, which would not ferment by itself, the movement by which the elementary atoms of the former are affected, is also transferred to the contiguous atoms of the latter, causing the elementary atoms in its compound molecules to enter into new combinations; and in this manner, the latter substance is made to resolve itself into new products. (Liebig.)

It appears, however, from the observations of many experimenters, and especially from the recent elaborate researches of Pasteur, that fermentation is never excited except under the influence of microscopic organisms, and moreover that each particular organism sets up a peculiar species of fermentation.

According to Schwann, the air contains the germs of microscopic plants and animals; and when these germs find a fitting soil, such as is offered by various nitrogenous bodies, they develop themselves therein, producing fungi and infusoria, which then, in a manner not yet explained, induce the fermentation of sugar, &c.

It appears also from the experiments of Schwann and of Helmholtz, that air which has been passed through a red-hot tube, and thereby freed from the germs of living organisms, cannot induce fermentation or putrefaction in nitrogenous bodies, and, consequently, that oxygen alone is not sufficient to bring nitrogenous matter into the condition of a ferment.

Blondeau also finds that fermentation in all its forms depends on the development of fungi. Alcoholic fermentation is excited by one particular fungus (*Torula cerevisiæ*); lactic fermentation by another (*Penicillium glaucum*). The latter fermentation takes place after the former, when a mixture of 30 grammes of sugar and 10 grms. yeast, with 200 cub. cent. water at the temperature of about 26° C., is left to itself for some time, after the termination of the vinous fermentation (which is completed in about two days). Beer-yeast mixed with a little water and left to itself in

a dark, moist place, was found to contain germs of *Torvula cerevisia* and *Penicillium glaucum*; when the liquid was filtered, the former of these remained on the filter and brought a solution of sugar into the state of vinous fermentation; but the latter being extremely small, ran through the filter, and the filtrate brought sugar-water into the state of lactous fermentation. *Acetous* fermentation depends on the development of *Torvula aceti*. The conversion of nitrogenous substances into fat (e. g. of casein in the preparation of Roquefort cheese, and of fibrin under similar circumstances), which Blondeau distinguishes by the term *fatty* or *adipic Fermentation* (*fermentation adipose*), is produced by *Penicillium glaucum* or *Torvula viridis*; and in butyrous fermentation and urinous fermentation (the conversion of urea into carbonate of ammonia), the action depends on the development of *Penicillium glaucum*. (Blondeau.)

Against this view Liebig raises the following objections:

Beer-yeast, which is supposed by Schwann, Turpin, and others, to consist of fungi, does not possess the composition of true fungi, but of gluten. It has never yet been specified in what manner these microscopic organisms effect the decomposition of fermentable substances. Are the products of fermentation and putrefaction the excrements of these living beings, to which the fermentable substance serves as food? Or do these organisms transform the original fermentable substance into new compounds (products of fermentation) by an external exertion of their vital force?—If vinous fermentation were a consequence of the more perfect development of fungi—as we might, perhaps, suppose to be the case in the fermentation of beer and wine—beer-yeast ought not to bring sugar-water into a state of fermentation, inasmuch as the sugar-water contains no nitrogenous matter which can serve as food to the fungi composing the yeast, but on the contrary these fungi disappear during the fermentation.—Sugar-water is likewise brought into the state of vinous fermentation by contact with cheese or almond-milk, though in this case no fungoid bodies are developed like those of the vinous ferment, as in the preparation of beer, or the fermentation of grape-juice.—In thousands of cases, no infusoria can be detected in putrefying cheese, blood, urine, or bile, or they do not make their appearance till the putrefaction has gone on for some time: hence they cannot be the cause of the putrefaction, but are merely developed from germs existing in the air, because these germs find nourishment in the putrefying substance. It is true that they then accelerate the decomposition, because they feed upon the organic matter, and convert it by their vital action into carbonic acid, &c. When they have thus consumed all the nutriment, they die, and serve as food for infusoria of other species. All this may take place when the air has access to the putrefying substance, but bodies which putrefy out of contact of air, cording for example, never exhibit infusoria, which, in fact, would be killed by the sulphuretted hydrogen evolved (Liebig). Liebig also remarks (*Handwörterbuch der Chemie*, iii. 217), that in the fermentation of milk, when that liquid is left to itself for a while in vessels containing air and bound over with blotting paper, till fermentation and formation of lactic acid are completely established, not a trace of vegetable growth can be detected. He moreover observes that in the study of fermentation, attention has been too exclusively directed to the vinous fermentation, and conclusions of too great generality have been drawn from the phenomena observed in that particular process, whereas, the explanation of vinous fermentation ought rather to be deduced from the study of fermentation in the more general sense.

C. Schmidt (Ann. Pharm. lxi. 168), is also of opinion that *fungi* are not the prime movers either in urinous (p. 634) or in vinous fermentation. He finds that the clear filtrate obtained by throwing almonds beaten up with water on a wetted filter, soon brings urea and grape-sugar into the fermenting state; and in the latter case, the fermentation may be in full play, although no trace of yeast-cells is discernible by the microscope, these cells not appearing till afterwards. If the saccharine liquid be left to itself for a week or a fortnight after the completion of the fermenting process, the groups of cells continue to grow in it, though no putrefaction takes place; the fungi, if washed and then introduced into a fresh solution of grape-sugar, grow in it vigorously, but excite only feeble and transient fermentation, if any: hence it appears that the growth of these plants is but a secondary phenomenon in fermentation.

R. Wagner, however (J. pr. Chem. xlv. 241), observed the simultaneous occurrence of fermentation and formation of yeast-cells under the conditions described by Schmidt.

On the whole, the question as to the exciting cause of fermentation and putrefaction, cannot be considered as quite decided; the balance of evidence appears, however, to be in favour of the view which regards the action of living organisms as essential to the commencement of these processes, as will appear from the details given in the following articles relating to vinous, lactous, and mucous fermentation; but it must still be admitted that we know nothing whatever of the mode of action of these organisms.

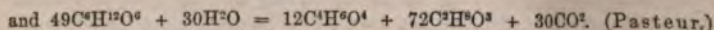
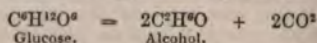


**FERMENTATION, ACETOUS.** The conversion of alcohol into acetic acid by atmospheric oxidation, is rather a case of *eremacausis* than of fermentation, and may take place under the influence of platinum-black, and other finely divided substances, which facilitate the transfer of oxygen; but as it is greatly accelerated by the presence of nitrogenous matter, and, according to Mulder, of a peculiar fungoid plant, the *Mycoderma Vini*, it is usually called *Acetous Fermentation* (i. 8).

Under this head may also be mentioned the conversion of citric and tartaric acids into acetic acid and some of its homologues, in contact with yeast or putrefying curd and a base, and even by mere exposure to the air (i. 995). Pasteur (Compt. rend. lvi. 416; Rép. Chim. pure, 1863, p. 221) has lately shown that tartrate of calcium mixed with a few thousandth parts of phosphate of ammonium and fixed alkaline or earthy phosphates,—when immersed in thoroughly de-aerated water and rigidly preserved from contact with the air, may be thrown into a state of active fermentation by the introduction of a very small quantity of the infusoria produced by the spontaneous fermentation of tartrate of calcium in contact with the air. The infusoria multiply rapidly at the expense of the tartrate which in a few days disappears entirely.

**FERMENTATION, ALCOHOLIC or VINOUS.** The clear juice of sacchariferous plants containing glucose,  $C^6H^{12}O^6$ , left to itself in contact with the air at temperatures between 20 and 24° C., becomes turbid after a few hours, gives off carbonic anhydride, becomes warmer than the surrounding air, and remains in a state of transformation from 48 hours to several weeks, according to the temperature, the amount of sugar present, and the nature of the nitrogenous matters, till, in fact, the whole of the sugar is decomposed. As soon as the evolution of carbonic acid is terminated, a substance previously suspended in it, the ferment or yeast (*Torula cerevisia*), separates, partly carried upwards by adhering gas-bubbles, partly downwards, leaving the liquid clear, which then, in place of the sugar, contains alcohol, glycerin, and succinic acid. The yeast formed in this process, if introduced at about the same temperature into a moderately dilute solution of pure sugar, induces therein also the decomposition of the sugar into the same products.

The formation of these products is represented by the following equations:



By far the greater part of the sugar is resolved into alcohol and carbonic anhydride, only about 4 or 5 per cent. being converted into succinic acid and glycerin. The formation of succinic acid in vinous fermentation was first observed by C. Schmidt, in 1847, and was communicated by him in a letter to Liebig (Handw. d. Chem. iii. 224). The formation of glycerin in this process was discovered by Pasteur.

Amylic alcohol is also frequently produced in the fermentation of sugar, and under certain circumstances tritylic, tetrylic, and according to Faget (?) hexylic alcohol. (See ALCOHOLS, i. 98.)

Cane-sugar,  $C^{12}H^{22}O^{11}$ , does not undergo vinous fermentation, till under the influence of a peculiar substance in the yeast, or of a substance contained in the kernel of fruits, it has been converted, with assumption of 1 at.  $H^2O$ , into glucose,  $C^6H^{12}O^6$  (see SUGAR). Milk-sugar is also converted into alcohol under the influence of putrid casein or gluten, and, under certain circumstances, of yeast, the formation of the alcohol being preceded, according to some observers, by the conversion of the milk-sugar into glucose. (See MILK-SUGAR.)

Solutions of sugar containing gluten altered by the process of germination or of mashing, undergo on standing an irregular fermentation, which however may be rendered regular by the introduction of a small quantity of yeast. Such is the case in the fermentation of beer-worts (Ure, J. pr. Chem. xix. 183). When albuminous substances, gluten, casein, or substances of like nature, are introduced into sugar-solutions, and the liquids are exposed for some time to the air, sometimes vinous fermentation takes place, sometimes another kind of decomposition.

A sugar-solution mixed with yeast ferments immediately, but the juice of grapes and other fruits requires access of air to bring it into the fermenting state.

Air previously heated to redness cannot induce fermentation in a solution of sugar, which has been mixed with yeast and then boiled, because, for the commencement of the process, either unboiled organic matter or unignited air which can supply the vegetable germs is necessary (Schwann, Pogg. Ann. xli. 187; Ure, J. pr. Chem. xix. 187). Wine-must, boiled and enclosed in a bladder, does not ferment even if suspended in fermenting must. It appears, indeed, that the access of a solid body from the air is essential to vinous fermentation, so that oxygen gas evolved from water by electrolysis is incapable of bringing boiled grape-juice into the fermenting state

(Helmholz, J. pr. Chem. xxxi. 434). The ferment of the air may likewise be retained by filtration through cotton; consequently sweet malt-wort in contact with filtered air does not ferment even for weeks. (Schróder and Dusch, Ann. Ch. Pharm. lxxxix. 332.)

Fresh grape-juice which has never come in contact with atmospheric air, suffers no alteration for years when kept over mercury at a temperature between 26° and 28° C. If oxygen gas previously heated to redness, or filtered through cotton be brought in contact with it, the juice after some hours becomes darker, absorbs the oxygen and gives off carbonic anhydride, but no fermentation takes place even after a long time. Common air, inasmuch as it contains bodies capable of forming yeast-cells, or the yeast-cells themselves (even such as have never been in contact with the air), can set up vinous fermentation, the continuation of which is promoted entirely by the growth of the yeast-cells. (Van den Broek, Ann. Ch. Pharm. cxv. 76.)

The fungi diffused over the surface of fruits, leaves, and fruit-stalks, likewise induce fermentation in saccharine liquids. If to a fermentable fruit-juice mixed with sugar, there be added 2 measures of water, the whole violently and continuously shaken, and the liquid which has become specifically lighter, set aside, the cells of the fungi rise to the surface, and there give rise to formation of mould, but no fermentation takes place within the liquid. (H. Hoffmann, Ann. Ch. Pharm. cxv. 228.)

If the moles floating in the air are collected in cotton or asbestos contained in a tube through which the air is drawn, and introduced into sugar-solutions which have been well boiled and cooled again, and are mixed with the mineral and albuminoid constituents of yeast, they develop into *infusorid* and *mucedineæ*, even if only ignited air has access to the liquid. Sugar-solutions mixed with the same yeast-constituents, but not containing this dust, undergo no alteration between 28° and 30° C., not even when cotton or asbestos alone is introduced into them. The same liquid remains unaltered if boiled in a glass flask, the neck of which is bent so that no dust can fall into it, the flask being afterwards left unclosed. (Pasteur, Compt. rend. l. 303.)

The better a saccharine liquid is adapted for the nutrition of yeast-cells, the more easily will they be developed (from the above-mentioned bodies in the atmosphere), when air has access to the liquid. Thus, vinous fermentation is almost always set up when the clear filtered wash-water or the decoction of yeast (which contains the soluble mineral and albuminoid constituents of that substance) is mixed with sugar-solution and left to itself (as observed long ago by Colin); it is frequently also accompanied by lactic fermentation; but the latter very seldom takes place alone, unless the wash-water of previously altered yeast has been used. (Pasteur.)

The vinous fermentation of sugar is likewise induced by the peculiar ferment of madder (Schunck's *erythrozym*) in contact with air, especially if this substance is in a state of decomposition. A mixture of carbonic anhydride and hydrogen is evolved, and the liquid after 14 days contains alcohol, acetic acid (perhaps also formic acid), a small quantity of succinic acid, and a sweet brown uncrystallisable body, probably glycerin, but no lactic acid. The same effect is likewise produced by the brown precipitate formed by adding a small quantity of hydrochloric acid to an aqueous infusion of madder after it has been rendered alkaline by lime-water. (Schunck, J. pr. Chem. lxiii. 222.)

Yeast consists of very small microscopic round or egg-shaped balls (Leuwenhoeck, Cagniard de Latour), of  $\frac{1}{1000}$  mm. diameter (Blondeau). These balls are vegetable cells (Cagniard de Latour), with elastic walls, filled with a liquid, and a soft, horny mass, which latter is at first attached to the walls, but extends to the middle as the cell grows. Young cells are transparent, and almost destitute of granular contents (Mitscherlich, Pasteur). These cells multiply by gemmation (Cagniard de Latour, Mitscherlich); the newly-formed cells do not separate from the central cell till they have attained to nearly the same size (Pasteur). They always remain isolated, and never form ramifications or elongated cells, like those of lactic ferment. (Blondeau.)

According to Cagniard de Latour, Turpin, and Mitscherlich, yeast-cells also increase by bursting and diffusing their granular contents through the liquid, the granules then developing into cells. Schlossberger and Pasteur did not observe this mode of formation, which is likewise inconsistent with the uniform size of the free yeast cells. Yeast contains cellulose, fat, nitrogenous and mineral substances. See analyses of yeast by Payen (*Mém. des Savants étrangers*, ix. 32); Dumas (*Traité de Chimie*); Mitscherlich (*Lehrb.* 4 Aufl. 370); Schlossberger (Ann. Ch. Pharm. li. 193).

The yeast deposited in the vinous fermentation of beer, of diabetic urine, of grape-juice, or other natural fruit juices, is invariably of the same composition (Quevenne, J. Pharm. xxiv. 265). In commercial beer-yeast, the cells of *Torvula cerevisia* and of *Penicillium glaucum* may be distinguished by the aid of the microscope. These two fungi may be separated one from the other, by washing and filtration, the larger cells



of the *Torula* remaining on the filter (and exciting vinous fermentation when introduced into sugar solutions), while the smaller cells of the *Penicillium* pass through the filter, and consequently the filtrate excites lactic acid fermentation in sugar-solutions. (Blondeau.)

On the distinction between top- and bottom-yeast, see the article BEER (i. 529); also Mitscherlich (Pogg. Ann. lix. 94), R. Wagner (J. pr. Chem. xlv. 241); on beer-yeast in general, Colin (Ann. Ch. Phys. xxx. 42).

Fermentation takes place only when the solution is sufficiently diluted with water, with less than 4 pts. water to 1 pt. sugar, it takes place but imperfectly or not at all, partly, perhaps, because the resulting alcohol precipitates the nitrogenous substances, destroys the fermentative power of the yeast, or renders the liquid unfit for its further development. If, on the other hand, the liquid is too dilute, the fermentation is slow, irregular, and easily passes into acetous fermentation. Moreover, it is necessary that the yeast be in direct contact with the sugar-solution: a solution of sugar contained in a bladder suspended within a fermenting liquid, does not ferment, but merely takes up a little alcohol by diffusion (Helmholz). When a tube plugged with filtering paper and containing yeast is introduced into a sugar solution, this solution passes through the paper, and ferments within the tube, but not outside (Mitscherlich, Ann. Chim. Phys. [3] vii. 7, 30). When a solution of sugar contained in a test-tube is separated into two parts by a cotton plug, and yeast is introduced into the upper part, this part ferments, but not the lower. (H. Hoffmann, Ann. Ch. Pharm. cxv. 228.)

An increase of yeast takes place in fermentation, when the liquid, in addition to sugar contains a nitrogenous substance. When, on the contrary, yeast is left in contact with a pure solution of sugar, it diminishes both in weight and in fermenting power and, in the end, becomes totally inactive. (Payen, Quevenne.)

In the fermentation of pure sugar solutions, the yeast first increases in weight and then diminishes; because it first assimilates the constituents of sugar, and gives them up again as the fermentation progresses. (Quevenne, J. Pharm. xxvii. 593.)

Yeast may grow and increase in sugar solutions, if they are mixed with ammoniacal salts, yeast-ash, and a trace of yeast, fermentation then also ensuing.

Yeast grows and multiplies in pure sugar solutions, as well as in such as have been mixed with albuminous substances. In the former case, all the yeast cells are found at the end of the fermentation to be deprived of their soluble nitrogenous constituents, which have been used for the formation of new yeast cells; in the second case there are found, together with the exhausted cells, a large number of newly-formed cells filled with soluble mineral and albuminoidal substances. (Pasteur.)

Sugar solutions containing a sufficient quantity of yeast ferment completely in two or three weeks, unless lactic fermentation takes place. But an extremely protracted fermentation ensues when yeast is mixed with excess of sugar. In this case the yeast lives at the expense of the soluble nitrogenous substances, and after these are used up, the younger cells continue to grow at the expense of the older. (Pasteur.)

During fermentation, part of the yeast is resolved into soluble products (Thénard). The yeast recovered from pure sugar solutions after fermentation is less rich in nitrogen than the original yeast, partly because its weight has been increased by the addition of non-azotised matter from the sugar, partly because a portion of its own nitrogenous substance has passed into the solution. On the other hand, it contains more cellulose and fat than before fermentation, which substances have therefore been formed from the sugar. The yeast formed in sugar solutions mixed with ammonia-salts, yeast-ash, and traces of yeast-cells, contains fat. (Pasteur.)

The nitrogen of yeast is not converted into ammonia during fermentation; on the contrary, any ammonia that may be added disappears wholly or partially. (Pasteur.)

When sugar solutions are fermented with a very large excess of yeast, the formation of alcohol and carbonic acid goes on, even after all the sugar is decomposed, at the expense of the non-azotised matter of the yeast, so that the amount of these two products obtained is more than equivalent to that of the sugar.

Yeast loses a considerable portion of its fermenting power by pressure, and still more by washing with water. After thorough drying, its power of exciting fermentation is, for the most part, destroyed: this statement is opposed to that of Cagniard de Latour. It likewise becomes inactive when heated, either alone or with water. Dried yeast excites fermentation even after cooling by solid carbonic acid (Cagniard de Latour). Yeast crushed on the grindstone no longer excites fermentation (Lüdersdorff, Pogg. lxxvii. 409), or only after a considerable time (Wagner); it then excites lactic fermentation (C. Schmidt). Yeast altered by too long continued putrefaction is inactive; but if the putrefaction has been less prolonged it may be checked and converted into fermentation by addition of sugar (Schlossberger, Ann. Ch. Pharm. li. 211). The fermentative power of yeast is destroyed by



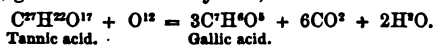
all substances which exert a poisonous action on fungi, but not by such as kill animals (Schwann, Mitscherlich, J. Pharm. [3] iv. 218). Yeast sprinkled with alcohol loses its fermentative power, which is not transferred to the alcohol.

The action of yeast on sugar is prevented by too great concentration of the solution, whether due to alkaline chlorides, gelatin, glycerin, or sugar (Berthelot, Ann. Chim. Phys. [3] l. 352). Strong mineral acids, added even in small quantity prevent the fermentation, phosphoric acid alone acting favourably. (Wagner, J. pr. Chem. xlv. 241.)

**FERMENTATION, AMYGDALOUS.** The conversion of amygdalin into bitter almond oil, hydrocyanic acid, and glucose, under the influence of emulsin or synaptase (i. 201).

**FERMENTATION, BUTYROUS.** See FERMENTATION, LACTOUS.

**FERMENTATION, GALLOUS or TANNOUS.** A solution of tannic acid exposed to the air, gives off carbonic anhydride, and is converted into gallic acid:



According to Stas (Ann. Ch. Pharm. xxx. 205) and Strecker (*ibid.* xc. 328), glucose is formed at the same time:



With pure tannic acid the action is extremely slow, but in infusion of galls, which contains the nitrogenous matter of the gall-nuts, it takes place quickly; still more so in gall-nuts merely moistened with water. The change may be regarded as a fermentation process, inasmuch as it is stopped or retarded by antiseptic substances, such as alcohol, wood-vinegar, creosote, and corrosive sublimate. According to Robiquet, the fermentation is excited by the pectase of the gall-nuts, which at the same time converts the pectose contained in them into pectin.

**FERMENTATION, LACTOUS.** When a solution of glucose, cane-sugar, or milk-sugar is mixed with fresh sour cheese, or with milk and chalk, and the mixture is exposed to the sun, or to a temperature of 25° to 30° C. for some weeks, with frequent stirring and renewal of the water as it evaporates, the sugar is converted into lactic acid, and ultimately, with evolution of hydrogen and carbonic anhydride into butyric acid, the acid uniting with the lime. As lactate of calcium is much less soluble than the butyrate, the conversion of the former into the latter may be recognised, when strong solutions of sugar are used, by the diminution of the crystalline mass produced at first.

Since glucose and milk-sugar contain  $\text{C}^{12}\text{H}^{24}\text{O}^{12}$ , and cane-sugar differs from them by only 1 at. water, the conversion of these sugars into lactic acid ( $\text{C}^4\text{H}^8\text{O}^4$ , or  $\text{C}^3\text{H}^6\text{O}^3$ ), consists merely in the splitting up of a molecule so constituted into two or more, and a new juxtaposition of the elementary atoms. The formation of butyric from lactic acid is represented by the equation:



In the preparation of lactic acid (as above), the precipitate formed on the bottom and sides of the vessel from the chalk and the products of decomposition of the cheese or milk is found, at the end of the fermentation, to be covered with a small quantity of a grey substance, the lactous ferment. When this substance is introduced into a cooled and clear-filtered decoction of beer-yeast, together with from 15 to 20 pts. of water, chalk, and a quantity of sugar equal to from  $\frac{1}{5}$  to  $\frac{1}{10}$  of the liquid, and this liquid is kept at a temperature of 30° to 35° C. for some days, a brisk evolution of carbonic anhydride and hydrogen takes place, the liquid becomes turbid and deposits a precipitate, and the chalk dissolves in the form of lactate of calcium. The new (and already purer) lactous ferment separated at this stage of the process, if introduced, together with chalk, into sugar-water, produces within an hour, an incipient evolution of gas and conversion of the sugar into lactate of calcium. (Pasteur, Ann. Ch. Phys. [3] lii. 404.)

This ferment, which appears to be necessary to lactous, as yeast is to vinous fermentation, is the *Penicillium glaucum*.

When lactous fermentation is set up in suitable sugar-solutions merely left to themselves, it is because certain bodies present in the air develop in the liquid, into cells of lactous ferment, which then set up the fermentation. If, therefore, the air is excluded, or only heated air has access to the liquid, no lactous fermentation will take place, unless lactous ferment is added. (Pasteur.)

Lactous ferment, viewed in the mass, resembles beer-yeast; it is grey, slightly glutinous, and appears under the microscope to consist of very small spherules of  $\frac{1}{300}$  mm. diameter; some isolated, others united in groups, and possessing molecular motion

(Pasteur). The cells of *Penicillium glaucum* have at most a diameter of  $\frac{1}{300}$  mm.; they increase at first, like the cells of yeast, by formation of new round cells, but afterwards by formation of elongated and many-branched cells, which ultimately cover the surface like a white mould. (Blondeau.)

A small quantity of lactous ferment is capable of decomposing a large quantity of sugar, provided the liquid is kept neutral by chalk; otherwise its action on the sugar is retarded by the free acid. It increases if nitrogenous matter, which may serve to nourish it, is likewise present. By desiccation or by boiling, with water, its action is weakened, but not altogether prevented. It acts best on sugar when air is excluded, inasmuch as the action is then not interfered with, either by the formation of mould, or by infusoria. If no other ferment is present, the lactous fermentation goes on regularly, and often more quickly than vinous fermentation. (Pasteur.)

In solutions of cane-sugar containing phosphoric acid and ammoniacal salts, the *Penicillium glaucum* can grow and convert all the sugar into lactic acid. (Pasteur, Compt. rend. li. 298.)

Previous to lactous fermentation, the liquid always becomes viscous, in consequence of the development of *Penicillium glaucum*, whose ramifications fill the liquid to such an extent, that it does not run out when the vessel is inverted. If this plant can develop itself in sugar solutions, lactous fermentation ensues, whether the liquid is acid or alkaline. If the liquid also contains albuminous substances, these yield ammonia and carbonic acid for the development of the *Penicillium*, and are partially converted into butyric acid, while part of the sugar is transformed into mannite. (Blondeau, J. Pharm. [3] xii. 257.)

The spontaneously developed fermentation of saccharine juices containing nitrogen, is sometimes lactous, sometimes vinous, most frequently both together. If yeast (as is generally the case) contains the cells of *Penicillium glaucum* as well as those of *Torula cerevisia*, vinous fermentation takes place first, then lactous fermentation at the expense of still unaltered sugar (Blondeau). When sugar solutions are brought into the state of lactous fermentation by cheese (or other nitrogenous substances), the lactic acid formed after a while prevents the further action of the ferment, but after repeated addition of acid carbonate of sodium (Boutron and Frémy), of chalk (Pelouze and Gélis), the whole of the sugar is converted into lactic acid. Slightly alkaline liquids are best adapted for the development of lactous ferment, neutral liquids for the development of yeast. (Pasteur.)

Sugar-solutions undergo lactous fermentation in contact with various membranes, especially calf's rennet (Frémy, Compt. rend. viii. 96, and ix. 165; see also Gay-Lussac, Compt. rend. ix. 46), with diastase altered by exposure to the air, with the previously altered nitrogenous substance of beet-juice, with decomposing animal bladder, with whey (Boutron and Frémy, Ann. Ch. Phys. [3] ii. 256; Blondeau). When urine mixed with sugar is left to itself, *Penicillium glaucum* becomes developed, and lactic acid is produced. (Blondeau.)

The soluble parts of gluten and casein, as well as the nitrogenous liquid which remains after vinous fermentation, are peculiarly well adapted for the development of lactous ferment; consequently, when these liquids are mixed with sugar and exposed to the air, lactous ferment is formed in them, even if yeast is added, the two ferments then exerting their specific actions side by side (Pasteur). See also MUCOUS FERMENTATION.

Aqueous sugar-solutions set aside for weeks or months at 40° C., a lower temperature in contact with chalk and cheese, glue, or other nitrogenous substances, undergo a fermentation different from the vinous, and not depending on the presence of yeast. In this fermentation, both the nitrogenous substance and the sugar are destroyed; carbonic acid, nitrogen, and hydrogen escape, and alcohol, lactate, and butyrate of calcium are produced. (Berthelot, Ann. Ch. Phys. [3] iv. 351.)

Berthelot designates this reaction *Fermentation alcoolique*, whereas Pasteur regards it as lactous fermentation.

**FERMENTATION, MUCOUS.** This is another kind of fermentation which sugar-cane undergoes, likewise under the influence of nitrogenous substances, and in contact with air; but under circumstances otherwise not exactly known, giving rise to the escape of carbonic acid and hydrogen, and the formation of mannite, a peculiar gum and a mucilaginous substance.

The mucous fermentation of sugar takes place (like vinous and lactous fermentation) under the influence of a peculiar mucous ferment. This ferment is composed of spherules from 0.0012 to 0.0014 mm. diameter, and when introduced into sugar-solutions containing albumin causes the sugar to be resolved into mannite, gum, and carbonic acid. 100 pts. cane-sugar yield, on the average, 51.09 pts. mannite, and 45.5 pts. gum, corresponding to the equation:



When a larger proportion of gum is obtained, the liquid is observed to contain larger spherules, probably belonging to a peculiar mucous ferment. (Pasteur, Bull. Soc. Chim. Paris, 1861, 30.)

Mucous fermentation requires access of air, and likewise the presence of nitrogenous matter; but the latter is capable of exciting mucous fermentation even after boiling. In this reaction, neither acid nor alcohol is produced. (Hochstetter.) Mucous fermentation is prevented by sulphuric acid, hydrochloric acid, or alum (Desfosses), by free mineral acids (Hochstetter, J. pr. Chem. xxix. 30).

The following are examples of this kind of fermentation:

Syrup of cane-sugar, which had been poured at the boiling heat into bottles in Martinique, the bottles being filled with it, underwent mucous fermentation on being transported to France, and poured out into open vessels. (Peligot.)

Fresh beet-juice becomes gummy by contact with air, and then contains mannite, gum, lactic acid, and uncrystallisable sugar. These changes take place with greater facility, when fermenting beet juice is added to the fresh juice, even when the greater part of the nitrogenous matter has been removed by lime, and whether the quantity of free alkali present is great or small. Alcoholic fermentation sometimes sets in if the acid is neutralised (Hochstetter). When carrot-juice is left to itself between 30° and 40° C., the cane-sugar which it contains is converted into glucose, mannite, lactic acid, and a gum isomeric with gum arabic. (Tilloy and MacLagan.)

The expressed juice of mangold-wurzel begins to ferment in 3½ days, and the fermentation is complete in 2½ days. From the solution clarified and evaporated to a syrup, alcohol of 80 per cent. precipitates a glutinous mucus, and the filtrate yields crystals of mannite. If the mucus be washed with alcohol, its aqueous solution precipitated with basic acetate of lead, the washed precipitate decomposed under water by sulphydric acid, and the filtrate evaporated to dryness, a transparent, slightly coloured gum is obtained. (Kircher, Ann. Pharm. xxxi. 337.)

The juice of the sugar-cane contains a white non-azotised (?) substance which becomes brown and moist in contact with the air, is soft and difficult to dry, soluble in water, insoluble in alcohol and ether, and is precipitated from its aqueous solution by oxide of lead, mercurous salts, and alcohol. It converts sugar into a substance intermediate between starch and gluten, this substance being formed quickly, and somewhat abundantly in syrups, and rendering them viscid, ductile, and uncrystallisable. If therefore, the juice, after being treated with lime, is left to stand for 48 hours, a jelly is produced, from which alcohol throws down a soft white nacreous precipitate, which dries up to a nacreous mass, dissolves but sparingly in hot or cold water, even when moist, but swells up in it to a transparent mass, and when treated with nitric acid, yields nothing but oxalic acid. This mass is not coloured by iodine, or converted into sugar by dilute acids, and does not give off ammonia on dry distillation. It is found abundantly at the bottom of the vats in which molasses is left to ferment for the preparation of rum. (Plagne, J. Pharm. xxvi. 248.)

Lemonade containing sugar, volatile oil, citric acid, and condensed carbonic acid, loses its fluidity, and becomes gummy by long keeping, especially in winter. If the gummy liquid be precipitated by alcohol, and the precipitate, which is friable when dry, washed with alcohol, there remains, after drying at 100° C., a viscid, semi-transparent, horny mass, while the alcohol takes up a brown uncrystallisable sugar. This mass recovers its former appearance when cold water is poured upon it, and forms with boiling water a gum which is difficult to filter, is not coloured by iodine, does not reduce potassio-cupric tartrate, or precipitate basic acetate of lead, and yields oxalic acid with nitric acid.

When yeast is well washed with cold water, then boiled with water, and ½ part sugar dissolved in the filtrate, the liquid after a few days becomes turbid and tenacious, like decoction of linseed. At the same time, a mixture of carbonic acid and carbonic oxide, in varying proportions, is evolved. This fermentation lasts about 12 days; for a shorter time, between 20° and 26° C.; it takes place also out of contact with air, and is excited even by yeast which has been boiled out with water (Desfosses, J. Pharm. xv. 602). Under similar circumstances, lactic fermentation may likewise take place. [On Mucous Fermentation, see also Vauquelin (Ann. Ch. Phys. xx. 93).]

Water boiled with gluten, produces in cane-sugar solution the same change as decoction of yeast. In contact with sugar-solution for 24 hours at 26° C., it gives off a smaller quantity of gas than the decoction of yeast, and renders the liquid gummy. The gaseous mixture contains hydrogen in larger proportion to the carbonic acid than that which is evolved by decoction of yeast. After the completion of the mucous fermentation, the liquid is still very sweet, but so thick that it runs out in threads when the vessel is inverted; when evaporated it leaves a non-crystallisable residue, and



on treating this with alcohol, a sacchariferous gum remains undissolved. If the remainder of the sugar be extracted from this gum by fermentation with yeast, there are obtained, for every 100 parts of sugar decomposed by the mucous fermentation, 109.48 parts of a pale yellow insipid gum, which yields scarcely any mucic acid when treated with nitric acid, is less soluble in water than gum-arabic, and yields a thicker mucilage than the latter. (Desfosses.)

**FERMENTATION, PECTOUS.** Many unripe fruits, fleshy roots, and other parts of plants contain a substance insoluble in water, alcohol, and ether (Fremy's pectose), which, during the ripening of the fruit, is converted, under the influence of a peculiar ferment called pectase, into various gelatinous substances which are soluble in water, viz. pectin, parapectin, and perhaps pectic acid in the ripe fruit, and metapectic acid in the over-ripe fruit. This is called pectous fermentation (Gm. xv. 393). See PECTIN.

**FERMENTATION, SACCHAROUS.** The conversion of starch into sugar under the influence of diastase (pp. 319, 625).

**FERMENTATION, SINAPOUS.** The formation of volatile oil of mustard from black mustard seed, by the action of myrosin on myronic acid (p. 624).

**FERMENTATION, TANNOUS.** See FERMENTATION, GALLOUS.

**FERMENTATION, URINOUS.** This term is applied to the conversion of urea in solution into carbonate of ammonia. Urea dissolved in pure water remains unaltered, but in the urine, which likewise contains mucus and other nitrogenous substances, it changes, with various degrees of rapidity, into carbonate of ammonia. In presence of yeast the change takes place very quickly. (C. Schmidt, Ann. Ch. Pharm. lxi. 168.)

**FERMENTATION, VINOUS.** (See p. 627.)

**FERMENTATION, VISCOUS.** Syn. with FERMENTATION, MUCOUS (p. 632).

**FERMENT-OILS.** (Gm. xiv. 403.)—These are volatile oils, produced by the fermentation of various plants, not originally contained therein, and essentially different from the oils which are extracted from unfermented plants by distillation with water. According to Becker (N. Br. Arch. lv. 161), they were known to the alchemists, and by them designated *quintessences*. Büchner (Repert. liii. 299), in 1835, first separated an oil of this nature from the fermented herb of *Erythræa Centaurium* by distillation. —Ferment-oils are for the most part much more soluble in water than ordinary volatile oils. According to Berzelius (Jahresber. xxvii. 541), they are perhaps peculiar alcohols, related to fusel-oil, and forming compound ethers with salt-radicles and acids.

1. *Ferment-oil of Charophyllum sylvestre.*—The flowering plant is left to ferment in water; the liquid distilled when the fermentation is ended; the distillate mixed with common salt, and shaken up with ether; and the ether removed from the aqueous solution and left to evaporate; the ferment-oil dissolved in it is then left behind. It is brown, lighter than water, with a strong and peculiar pungent odour, and an aromatic taste, not bitter, but slightly scratching. Evaporates quickly even at 18° C.: burns, when set on fire, with a clear, luminous flame, diffusing a vapour which excites coughing.—*Chlorine-water* converts it into yellow flocks retaining the odour of the oil. It dissolves iodine. It is decomposed with violence by *nitric acid*. By *oil of vitriol* it is coloured brown, without losing its odour; the solution is rendered milky by water. It forms an emulsion with *aqueous ammonia*, dissolves sparingly in *water*, easily in *alcohol*, *ether*, and *oils*, both *fixed* and *volatile*. It dissolves resin. (Bley, N. Br. Arch. xlv. 50.)

2. *Ferment-oil of Chelidonium majus.*—Obtained from the roots, in the same manner as the ferment-oil of *Charophyllum sylvestre*. Lighter than water; has an agreeable odour like the bouquet of wine, and a persistent, biting taste. It is not very volatile. With *iodine* it forms a violet solution. With *nitric acid* it evolves nitrous gas, and with *sulphuric acid* it forms a slightly coloured solution which is scarcely clouded by water. It dissolves sparingly in *water*, readily in *alcohol*, *ether*, and *oils*, both *fixed* and *volatile*. (Bley, N. Br. Arch. xlviii. 156.)

3. *Ferment-oil of Conium maculatum.*—Obtained from fresh hemlock in the same manner as the ferment-oil of *Charophyllum sylvestre*. Colourless; has a peculiar odour, not like that of hemlock, and a sharp, burning taste; it is not poisonous. Dissolves with facility in *alcohol*, *ether*, and *oils*, both *fixed* and *volatile*. (Landerer, Repert. xlv. 237.)

4. *Ferment-oil of Erythræa Centaurium.*—The plant, after maceration in water for 12 hours, gives off a perceptible odour, which increases up to 60 hours maceration and then ceases (Büchner.) The aqueous distillate is pale-yellow, with white turbidity;

has a persistent enlivening aromatic odour, which is not pleasant when close, and irritates the eyes and nose; its taste is excessively burning, like that of crocote, but not persistent. It reddens litmus, but not permanently (Büchner, *Repert.* liii. 303), and when heated with ammonia and nitrate of silver, reduces the solution to the metallic state (Büchner). To prepare the oil, the fresh herb is macerated in water for 48 hours, the whole distilled, the odoriferous distillate redistilled, and this process continued as long as drops of oil pass over with the watery vapour. It is a thin greenish oil, having a peculiar, but not disagreeable odour; it is not poisonous. (Büchner, *Repert.* liii. 299.)

5. *Ferment-oil of Echium vulgare.*—The plant in the flowering state is distilled with water after maceration; the distillate is shaken up with ether, and mixed with common salt; and the ether decanted therefrom is distilled off. Pale yellow oil lighter than water, and smelling like other ferment-oils. Easily soluble in alcohol and in ether. (Bley, N. Br. Arch. xxx. 167.)

6. *Ferment-oil of Erica vulgaris.*—The fresh herb is distilled after maceration with water; the distillate is cohobated and repeatedly distilled after addition of common salt, then shaken up with ether as long as the ether acquires any odour; and the ether is carefully distilled off from the dissolved oil. The oil obtained amounts to 0.023 per cent. Greenish-yellow, mobile, lighter than water, with a peculiar odour, and a sweetish, aromatic, burning taste; reddens litmus. When set on fire, it burns with a clear, blue-edged flame, without leaving any residue. It is not deodorised by chlorine-water. It dissolves iodine without detonation. With fuming nitric acid, it froths up, and the solution mixed with water deposits resinous flakes. With sulphuric acid, it becomes darker, without losing its colour. (Bley, N. Br. Arch. xxi. 302.)

7. *Ferment-oil of Marrubium vulgare.*—The comminuted herb is soaked in water and exposed to the sun, whereby it acquires an offensive odour; the liquid is then distilled; the distillate saturated with common salt; the flocks thereby separated are collected on a filter and dissolved in ether; and the ether is left to evaporate slowly. The distillate saturated with common salt yields, when heated, a second aqueous distillate from which the oil may be extracted by agitation with ether. It is lighter than water; has a peculiar sweet, ethereal odour, and an aromatic, slightly biting taste. When set on fire it burns with flame, without leaving charcoal. It dissolves in dilute nitric acid, and yields a bitter substance with strong nitric acid. With sulphuric acid it becomes heated and acquires a peculiar odour. With chlorine-water it emits an odour of roses and forms a film of resin. It dissolves in aqueous alkalis and in water. (Bley, N. Br. Arch. x. 67.)

8. *Ferment-oil of Achillea Millefolium.*—The fresh flowering plant is macerated in water, and left to ferment; the whole is distilled, with cohobation; the blue oil which floats on the distillate is removed; the residual water, after addition of common salt, is agitated with ether; and the ether which separates is left to evaporate. Yellow-brown oil, having a slightly aromatic odour, and an aromatically bitterish, rather sharp taste. It dissolves in alcohol, ether, and oils, both fixed and volatile. (Bley, N. Br. Arch. xxx. 167.)

9. *Ferment-oil of various species of Plantago.*—Obtained from plantain-leaves by fermentation, distillation, and agitation of the distillate with ether, in the same manner as the ferment-oil of *Achillea Millefolium*. It is yellow, transparent, has an ethereal odour slightly resembling that of mustard-oil, and an aromatic, sweet, burning taste. Very volatile. With fuming nitric acid it turns brown, with rise of temperature and intumescence; the solution first becomes greenish-yellow with milky turbidity, then clear, smells like artificial musk, and has a disgustingly bitter taste. With sulphuric acid it forms a dark brown-red mixture, from which water separates resinous flocks smelling of resin and ferment-oil. It dissolves in alcohol, ether, and oils. (Bley, N. Br. Arch. xl. 130.)

10. *Ferment-oil of Quercus Robur.*—Obtained from fresh oak-leaves by fermentation, distillation, and treatment of the distillate with ether in the same manner as the ferment-oil of *Achillea Millefolium*. Pale green. Specific gravity 0.695; has an agreeably enlivening odour, a sweet, burning taste, and reddens litmus. It is easily inflammable, burns with penetrating odour, and with a first bluish, then whitish, non-fuliginous flame. With fuming nitric acid it froths up and becomes very hot, but does not lose its odour. With sulphuric acid it becomes hot and assumes a dark red-brown colour. It dissolves sparingly in water, readily in alcohol, ether, and oils, both fixed and volatile. (Bley, N. Br. Arch. xxvi. 48.)

11. *Ferment-oil of Salix pentandra.*—Obtained from fresh willow-leaves in the same manner as the ferment-oil of *Achillea Millefolium*. Yellow, lighter than water; has an aromatic odour, like that of castoreum, and at the same time like that of willow-leaves; reddens litmus. Smells strongly when heated, and burns, when set on fire, with a very smoky flame, leaving a small quantity of charcoal. Dissolves iodine

abundantly. With *fuming nitric acid* it froths up and thickens, but does not take fire.

12. *Ferment-oil of Scilla proserpina*.—Obtained from the fresh herb, like the ferment-oil of *Achillea Millefolium*. Dark red-brown, with a repulsive, ethereal, sweetish odour, and an aromatic taste. It dissolves sparingly in water, easily and in all proportions in alcohol, ether, and oils, both fixed and volatile. It forms a liniment with aqueous ammonia, and is very sparingly dissolved by aqueous potash. (Bley, N. Br. Arch. li. 257.)

13. *Ferment-oil of Trifolium Strium*.—Obtained like the ferment-oil of *Achillea Millefolium*, from the dried plant, even after it has been well boiled with water and no longer has a bitter smell, by fermentation, distillation, saturating the distillate with common salt, and shaking it up with ether. It is pale yellow, lighter than water, smells strongly aromatic, like the ferment oil of *Tussilago farfara*; its taste is at first burning and sweetish, afterwards aromatic. When set on fire, it burns with a blue, slightly fuliginous flame, giving off strong-smelling vapours which excite coughing, and leaves a small quantity of charcoal. It dissolves sparingly in water, easily in alcohol and ether. (Bley, Jahrb. pr. Pharm. ii. 207.)

14. *Ferment-oil of Tussilago farfara*.—The fresh bruised herb is macerated in water for 10 or 12 days, during which it turns light green, and acquires the odour of pickled gherkins; the whole is then distilled; the distillate, which has a vinous odour is saturated with common salt and redistilled; this second distillate is shaken up with a large quantity of ether; and the ether is taken off and evaporated, the dissolved oil then remaining behind. Yellowish, lighter than water, very volatile, with a peculiar, strongly aromatic, penetrating odour, and an aromatic taste, neither burning nor cooling. It easily takes fire and burns at first with a whitish, afterwards with a reddish, sooty flame. It dissolves iodine abundantly, dissolves in sulphuric acid with yellowish colour, without losing its odour, and turns brown when heated with it. With potash it is said to form a whitish soapy compound. It dissolves sparingly in water, readily in alcohol and ether. (Bley, Rept. lxii. 406.)

15. *Ferment-oil of Urtica urens*.—Obtained like the ferment-oil of *Achillea Millefolium*, from the flowering plant, which, during fermentation, emits, first a vinous, then a sharp and intoxicating odour. Resembles the ferment-oil of *Echium vulgare*. (Bley, N. Br. Arch. xxx. 167.)

16. *Ferment-oil of Vitis vinifera*.—Fermented vine-leaves are distilled; the distillate is cohobated and shaken up with ether; the ethereal solution is distilled; and the ethereal, peculiar-smelling distillate is rectified; the ferment-oil dissolved in it then remains behind. Pale yellow, lighter than water; has a peculiar vinous odour, like vine-flowers and mignonette, and a burning, sweetish, aromatic taste. It reddens litmus slightly but permanently. It evaporates in the air, diffusing a strong odour. Heated with *fuming nitric acid*, it resinises and assumes a grass-green colour. With sulphuric acid, it forms first a white, then a light-red, and ultimately a brown mixture, without losing its odour. It is not deodorised by agitation with chlorine water. With aqueous potash it forms a clear mixture, from which the oil afterwards separates, with red-brown colour, but with its original odour. It dissolves sparingly in water, without alteration in hydrochloric and acetic acid. With sulphide of carbon it forms a milky liquid, from which it afterwards separates unaltered; with carbonate of potassium, a liniment from which it also separates unaltered; with aqueous ammonia a soapy mixture. It dissolves abundantly in alcohol, ether, and fixed oils; in oil of turpentine and oil of lemon, it forms at first a milky solution, which afterwards becomes clear. (Bley, Rept. Pharm. lxviii. 301.)

An oil, different from that just described, may be obtained from wine, by leaving it to freeze, distilling off the volatile part of the remaining liquid, and shaking up the residue with ether. (Bley.)

17. *Ferment-oil of diseased Apples*.—*Malöl, Oil of Apples*.—Produced in cellulosis, a disease of the apple, which imparts a musky odour to that fruit. It is obtained from the diseased apples by distillation with water. Yellowish-grey, lighter than water; boils at 109° C. Smells of musk, tastes rough and sharp. Contains 64.15 per cent. C, 20.65 H, 15.15 O, and 0.05 N. It volatilises completely when heated, and burns, when set on fire, with a feeble flame, diffusing a small quantity of smoke. Chlorine decomposes it, with elimination of hydrochloric acid. With dry hydrochloric acid gas, it forms a crystalline compound (*Chlorhydrate de Malöile*). It dissolves readily in alcohol and ether, and imparts a musk-like odour to water. (Rossignon, J. Pharm. xvii. 158.)

**FERRATES.** Salts containing iron, analogous to the manganates, and therefore represented by the general formula  $M^2O.Fe^2O^3$ , or  $MFeO^2$ . They are very unstable, and only the potassium- and barium-salts have been examined.

*Ferrate of Potassium* was first prepared by Frémy in 1840 (Ann. Ch. Pharm. xl.



261; xlv. 254), and has been further examined by H. Rose (Pogg. Ann. lix. 315) and J. Denham Smith (Phil. Mag. [3] xxiii. 217). But, according to Kopp (*Geschichte der Chemie*, i. 192), Stahl appears to have observed that iron calcined with nitre yields with water a purple or amethyst-coloured solution. Eckeberg also observed, in 1802, that the mass obtained by fusing gadolinite with hydrate of potassium yields with water a dark-red alkaline solution, the colour of which proceeded, not from manganese, but from iron, and Becquerel in 1832 (Ann. Ch. Phys. [2] li. 105) remarked that ferric oxide fused with hydrate of potassium gives off oxygen, which he attributed to the decomposition of peroxide of potassium.

Ferrate of potassium is prepared: 1. By projecting a mixture of 1 pt. iron-sfilings, and 2 pts. nitre into a capacious crucible kept at a dull red heat, and removing the crucible from the fire as soon as the mixture begins to deflagrate and form a white cloud; if the heat is too strong, the compound decomposes as fast as it is formed. The soft, somewhat friable mass of ferrate of potassium thus obtained may be taken out with an iron spoon and preserved in well-stoppered bottles. Or the salt may be obtained in solution by treating the fused mass with ice-cold water, leaving the liquid to stand, to allow the undissolved ferric oxide to settle down, and then decanting; the solution must not be filtered, as it is immediately decomposed by contact with organic matter.—2. By igniting ferric oxide with hydrate of potassium in an open crucible, or with a mixture of hydrate of potassium and nitre.—3. By passing chlorine gas through a very strong solution of caustic potash containing hydrated ferric oxide in suspension, fragments of solid potash being continually added to maintain a large excess of alkali in the liquid. The ferrate of potassium, being almost insoluble in the strong alkaline liquid, is deposited in the form of a black powder, which may be freed from the greater part of the mother-liquor by drying it on a plate of porous earthenware (Frémy).—4. By electrolysis. A cylinder of porous earthenware is filled with strong potash-ley and placed within a beaker-glass containing the same liquid. A cast-iron plate connected with the positive pole of a powerful voltaic battery dips into the liquid outside the porous cylinder, and a plate of iron or platinum connected with the negative pole is immersed in the liquid within the cylinder. The whole of the liquid is cooled as much as possible by surrounding the beaker with ice. The potash-solution surrounding the positive pole quickly assumes a red colour, and after a while becomes dark and opaque; sometimes also the positive plate becomes coated with microscopic crystals of ferrate of potassium. (Poggendorff and Rose, Pogg. Ann. lix. 315.)

Ferrate of potassium is soluble in water, less soluble in presence of potash. The deep cherry-red solution is, when concentrated, transparent only in thin layers. In the concentrated state, and when mixed with free potash, it may be preserved for some time, and may even be boiled without decomposition, but the more dilute and the warmer the solution is, the more easily does it decompose, with evolution of oxygen and precipitation of ferric oxide; a dilute solution is constantly decomposed by boiling. Acids, even nitric and sulphuric acid, decolorise the red solution immediately, with evolution of oxygen, and if only a small quantity of acid is present, with separation of ferric oxide; with hydrochloric acid it gives off chlorine. The solution is decomposed by metals, and by many metallic salts, including alum; from salts of manganese and nickel, it throws down peroxides of these metals. It is quickly decomposed and decolorised by deoxidising substances, such as sulphurous acid, nitrous acid, ammonia, ammoniacal salts, and especially by organic bodies. Sulphydric acid and sulphide of ammonium impart to the concentrated solution a dark green colour, becoming light green on dilution with water, brown when heated, green again on cooling; in this reaction a sulphur-salt appears to be formed, containing a polysulphide of iron analogous to ferric acid.

By passing sulphurous acid gas through the aqueous solution till the colour is destroyed, and determining the quantity of ferric oxide precipitated, and of sulphuric acid produced (by supersaturating the filtrate with hydrochloric acid and precipitating with chloride of barium), it is found that 699 pts. (3 at.) sulphate of barium,  $\text{BaSO}_4$ , correspond approximately to 160 pts. (1 at.) ferric oxide,  $\text{Fe}_2\text{O}_3$ . Hence ferrate of potassium is  $\text{KFeO}_2$  or  $\text{K}'\text{O}.\text{Fe}'\text{O}_2$ , and the decomposition is represented by the equation:



Consequently, ferric acid, if it could be obtained in definite form, would be  $\text{HFeO}_2$ , or  $\text{H}'\text{O}.\text{Fe}'\text{O}_2$ , and ferric anhydride  $\text{Fe}_2\text{O}_3$ . (H. Rose.)

*Ferrate of sodium* is obtained similarly to ferrate of potassium. The other salts, which are insoluble, are obtained by precipitation.

*Ferrate of barium*,  $\text{BaO}.\text{Fe}_2\text{O}_3$  +  $\text{H}_2\text{O}$  (?), or  $\text{BaFeO}_2$  +  $\frac{1}{2}\text{aq.}$  (?), is obtained by decomposing the potassium-salt with chloride of barium, as a bulky cochineal or purple-red precipitate, becoming brick or rose-red after washing and drying at  $100^\circ\text{C}$ . It is tolerably stable, may even be boiled for a while with water, and dissolves with red

colour in acetic acid; but by nitric or sulphuric acid, or by strong heating, it is immediately decomposed and decolorised. (Denham Smith.)

**FERRIC ACID**, or *Ferrate of Hydrogen*, has not been obtained in definite form, or even in aqueous solution, as it decomposes and gives off oxygen as soon as liberated from its salts by the action of an acid (p. 637).

**FERRIC OXIDE**. *Sesquioxide of Iron*.  $\text{Fe}_2\text{O}_3$ . See IRON.

**FERRIC SALTS**. *Sesquisalts of Iron*. See IRON, and the several ACIDS.

**FERRICYANIDES** or **FERRIDCYANIDES**. See CYANIDES OF IRON (p. 243).

**FERRITES**. Compounds of ferric oxide with alkalis. (See IRON, OXIDES OF.)

**FERROCOBALTINE**. Cobaltine,  $\text{Co}^2\text{AsS}$ , in which a considerable proportion of the cobalt is replaced by iron. (See COBALTINE, i. 1057.)

**FERROCYANIDES**.

**FERROPRUSSIATES**.

} See CYANIDES OF IRON (p. 222).

**FIBRIN** is the name given to the substance which is separated in the solid state from blood on coagulation. A similar matter is contained in the solid muscular flesh of animals, but differs from blood-fibrin in certain properties. Lehmann has named this fibrous substance *syntonin*. Fibrin is also contained in lymph.

1. *Preparation*.—Fibrin may be obtained immediately by lashing fresh blood with a bundle of birch-twigs; it attaches itself to the twigs in amorphous, fibrous filaments, which retain a red-colour from adhering blood globules. In order to free the fibrin from colouring and other matters, it is placed on a sieve or a cloth and subjected to prolonged washing under a copious stream of water, and the portions which retain the red colour most obstinately are picked out and thrown aside. It is finally washed with distilled water charged with carbonic acid. A few drops of acetic acid may be advantageously added to the last wash-waters; this causes the fibrin to swell up, and renders it easier to distinguish the impure portions. The product, finally washed with pure water, assumes the semi-transparent, fibrous aspect, peculiar to fibrin. (Gerh. iv. 459.)

When fresh blood is allowed to stand, it coagulates spontaneously, the clot, at the same time, enclosing all the blood-globules. It is therefore necessary to cut the clot into thin slices, and wash it with still greater care than artificially coagulated fibrin. Fibrin obtained by either method always contains many impurities, especially fat-globules; these may be removed by ether and alcohol, after the product has been dried.

Gerhardt recommends the following method for preparing fibrin in a state approaching to purity. The blood, as it leaves the veins, is allowed to flow upon the twelfth or fifteenth of its weight of moist sulphate of sodium, which prevents the fibrin from coagulating. The mixture is agitated and thrown on a filter, which retains by far the greater part, if not all the globules. If the filtrate is slightly red, it is mixed with an equal volume of water, and again filtered; and this process is repeated till the liquid begins to deposit fibrin. The fibrin is then collected, strained off, and washed with water, alcohol, and ether.

Liebig prepares muscular fibrin (*syntonin*) by finely mincing fresh meat, and exhausting with cold water. The residue is then treated with water containing 0.1 per cent. hydrochloric acid, and the solution is filtered and neutralised with ammonia. The fibrin is purified in the usual manner.

Baumhauer uses fish for preparing *syntonin* (*Chemische Unters. v. Mulder*, German transl. iii. 301), but the method does not appear to be advantageous.

*Impurities*.—Fibrin is generally mixed with fat-globules, but only such as are found adhering to the different constituents of blood. Lehmann discovered cholesterol in this fat, also acetic acid, perhaps formed by the oxidation of ether, and another fatty acid (*Gmelin's Handbuch*, viii. [2] 171). Fat always adheres to fibrin, and appears to consist principally of ammonia- and lime-soaps (Berzelius, *Lehrb. d. Chem.* ix. 88). Schmidt extracted from 7.4 to 8.7 per cent. fat from the fibrin of the blood of the portal vein. Lehmann found between 3.189 and 3.218 per cent. of fat in fibrin (*Gmelin's Handbuch*, viii. [2] 141). Virchow extracted, by means of alcohol and ether, between 2.50 and 2.76 per cent. fat from venous fibrin. The fibrin of chyle is richer in fat than blood fibrin. Virchow found phosphoglycerate of calcium in blood-fibrin, and much phosphate of calcium in its ash. Fibrin always leaves a mineral residue on incineration, consisting chiefly of phosphate of calcium, amounting to 1.7 per cent. (Mulder), 0.66 per cent., with a little carbonate of calcium (Virchow). A little phosphate of magnesium is likewise found in the ash, but no iron when the fibrin has been properly purified. According to Liebig, the ash of *syntonin* always contains iron. Fibrin of the arterial blood of the horse contains 2.172 per cent. ash; that of the

jugular blood 1·907 per cent. In chyle-fibrin, which had been properly freed from fat, washed, and dried, 1·77 per cent. strongly alkaline ash was found (Lehmann). Virchow thinks it probable that the fat adhering to fibrin contains *myelin*, a substance which he considers to be identical with nerve-marrow, and to bear a certain resemblance to cerebrie acid. It is found in various normal and morbid structures; when treated with water, it swells up like starch.

*Formation of Fibrin from Albumin.*—When defibrinated serum is subjected to the action of a current of oxygen gas, at a temperature of 98°—100° Fahr., the albumin contained in it is gradually converted into fibrin\*, which separates after about 36 hours in clots, and when freed from blood-cells and other impurities by washing with water, presents the appearance of ordinary fibrin. A similar result is obtained when a mixture of blood-serum and egg-albumin is treated with oxygen gas, time being allowed for the two liquids to mix well together. Egg-albumin alone, when purified by beating it up with a small quantity of acetic acid, and filtering, also yields fibrin when a stream of oxygen is passed through it. The introduction of coils of platinum wire into the liquid greatly facilitates the formation of the fibrin, which is then deposited on the coils in beautiful white parallel threads. Alkalis and alkaline salts interfere with the production of fibrin in the manner above described, the greatest amount being obtained when the albumin is neutral or slightly acid. Viscidity of the liquid promotes the formation of fibrin by detaining the bubbles of oxygen for a longer time among the particles of the albumin. Albumin artificially digested in gastric juice yields fibrin by oxidation, even after it has been passed through a dialyser. *Gluten* dissolved in gastric juice also yields fibrin by oxidation, even at ordinary temperatures. (A. H. Smeë, Proc. Roy. Soc. xii. 399.)

*Properties.*—Fibrin has been said to separate from the blood in laminae. This is not certain, but when completely washed, it consists of soft, elastic, transparent filaments, which do not cohere by pressure. It is completely insoluble in cold water, in alcohol, and in ether.

Freshly prepared fibrin loses about 80 per cent. water in vacuo (Chevreul), and is converted into a hard, horny, transparent mass, of yellowish or greenish colour, and completely devoid of taste and smell. It takes up about three times its weight of water, without, however, entirely regaining its former appearance. When well-washed fibrin is boiled for a long time with water, the distillate contains much ammonia, and a peculiar substance is extracted from the residue by water (Dumas and Cahours). The substance extracted from fibrin by boiling water, has, according to Bouchardat, all the properties of gelatin; the proportion varies considerably, being insignificant in healthy fibrin, but increasing to a considerable amount in inflammatory diseases of the cellular tissue. The substance obtained by Dumas and Cahours did not become gelatinous on cooling, but appeared to resemble albumin; it was precipitated by tannin and nitric acid, contained 11 per cent. ash, and the organic part gave 47·9 per cent. C, 6·8 per cent. H, 15·0 per cent. N, and 30·3 per cent. O.

Heated with water in a sealed tube to 150° C., fibrin dissolves almost completely, leaving a slight residue. The solution produces abundant precipitates with acids, and even when very dilute, is precipitated by nitric acid. The precipitate produced by acetic acid is readily soluble in an excess of the acid.

When moist fibrin is exposed to the air, it is gradually converted into a thick viscid liquid, smelling like old cheese. This liquid coagulates by heat; the coagulum has the composition and properties of albumin (C 53·9, H 7·0, N 15·6, S 1·6 per cent.; ash 0·28 per cent. Strecker). Putrefying fibrin also yields sulphide of ammonium, butyric and valeric acids; leucine; an oily acid precipitated by acetate of lead; an acid syrup which is dissolved by acids, thereby assuming a violet colour and being converted into tyrosine; and a crystalline volatile substance of unpleasant odour (Bopp, Ann. Ch. Pharm. lxi. 30). When fibrin putrefies out of contact with the air, it yields acetic, butyric, valeric, and capric acids, as well as ammonia (Brendecke). Fibrin, in contact with oxygen, gives off carbonic acid; and fibrin, which has been long exposed to the air, and perhaps also fibrin from arterial blood, dissolves with difficulty or not at all in saline solutions. Peroxide of hydrogen is decomposed by fibrin. If fresh fibrin, moistened with water and saturated with oxygen, is enclosed in 8 times its volume of air, and maintained between 20° and 25° C., the gas, after 24 hours, contains 6·81 per cent. O, 11·17 CO<sub>2</sub>, and 82·02 N.

Fibrin has been analysed by a great many chemists; the results are not sufficiently in accordance to lead to the conclusion that it is a homogeneous substance. It appears to vary considerably in composition, according to the source from which it has been obtained.

\* A black substance, analogous to if not identical with Virchow's *Aerwin*, is formed at the same time.



## FIBRIN.

	From human venous blood.			From bullock's blood.			
	Scherer.	Dumas and Cahours.		Gay-Lussac and Thenard.	Schlossberger.	Dumas and Cahours.	Verdeil.
Carbon .	53.7	54.3	52.8	53.4	52.4	52.7	
Hydrogen .	7.1	7.2	7.0	7.0	6.9	7.0	
Nitrogen .	15.8	15.8	16.8	19.9	15.5	16.6	
Sulphur .	.	.	.	.	.	.	1.6
Oxygen .	.	.	.	.	.	.	

	Arterial and venous blood of sheep.		Dumas and Cahours.		
	Dumas and Cahours.	Flesh of sheep. Strecker.	Arterial and venous blood of Calf.	Horse.	Dog.
Carbon .	52.8	.	52.5	52.7	52.7
Hydrogen .	7.0	.	7.0	7.0	6.9
Nitrogen .	16.5	16.8	16.5	16.6	16.7
Sulphur .	.	1.1	.	.	.
Oxygen .	.	.	.	.	.

	Flesh of sheep. Strecker.	Dumas and Cahours.	
		Fibrin boiled with water.*	Fibrin dissolved in potash and precipitated by acetic acid.
Carbon .	54.7	53.5	53.1
Hydrogen .	7.2	7.1	7.1
Nitrogen .	15.4	15.9	16.8
Sulphur .	1.5	.	.
Oxygen .	.	.	.

Mulder (*Chemische Untersuchungen*) gives, for the composition of fibrin, 52.7 per cent C, 6.9 H, 16.4 N, 1.2 S, 0.3 P, and 23.5 O. Comparing this result with the analysis of blood-albumin by the same chemist (i. 67), it will be seen that the oxygen in fibrin exceeds that in albumin by 1.5 per cent, the quantities of the other elements being proportionally less. This difference is quite in accordance with the fact observed by Smeee (p. 639), that albumin is converted into fibrin by oxidation, with separation of sulphur, phosphorus, and carbonic acid. On the other hand, it must be observed, that, according to the analyses of other chemists, albumin and fibrin do not present any essential difference of composition: indeed, the analyses of each of these substances by different chemists (see above and i. 67), differ from one another quite as much as the analyses of either substance differ from those of the others. If they are really identical in composition, the conversion of albumin into fibrin by the action of oxygen, must be regarded as a case of contact-action.

According to MM. Lebonite and Goumoens, fibrin is composed of two bodies; exhibiting, under the microscope, yellowish-white fibres, parallel and wavy on the sides, as well as very numerous granulations disseminated upon the surface of its fibres and enclosed by them. (Gerh. iv. 464.) See p. 641.

*Decompositions.*—1. Fibrin is decomposed at a high temperature; it melts, swells considerably, takes fire and burns with a smoky flame, leaving a residue of porous charcoal. By dry distillation, it yields the same products as albumin.

2. Fibrin dissolves in *caustic potash*, even in very dilute solutions; at first it swells up and becomes gelatinous, and between 50° and 60° C. gradually dissolves, forming a slightly opaline yellow solution, which becomes clear on filtration. Fibrin does *not neutralise* the alkali, but decidedly lessens its alkaline properties; the solution has the characteristic of albuminate of potassium, yielding precipitates with acetic and with tribasic phosphoric acids, soluble in excess of the precipitant. According to Mulder, if fibrin is digested with very weak alkali, and the solution neutralised with acetic acid till it begins to be precipitated, compounds with metallic oxides may be obtained on the addition of their salts. Gerhardt thinks that these precipitates are identical with the metallic albuminates (i. 68). When fibrin is boiled with caustic potash, ammonia is evolved, and the liquid contains sulphide of potassium. Heated with potash-lime between 160° and 180° C., it evolves ammonia and other volatile products, while a small quantity of a volatile fat acid is formed, which remains combined with potash (Wurtz). When fused with potash, it yields hydrogen and ammonia, leucine, tyrosine, and probably butyrate, valerate, oxalate, &c., of potassium. (Bopp.)

3. Fibrin is scarcely acted upon by *ammonia*.

4. Concentrated fuming *hydrochloric acid* causes fibrin to swell, and dissolves it when heated, forming a violet solution. When this solution is boiled in an open vessel, it

\* Appears to have lost nitrogen in the form of ammonia.

turns brown, and is then found to contain chloride of ammonium, leucine, tyrosine, a brown substance not yet examined, an uncrystallisable body slightly soluble in water and very soluble in alcohol, and a sweet syrupy matter (Bopp). According to Mulder, fibrin absorbs 7.1 per cent. of gaseous hydrochloric acid, yielding a compound almost insoluble in water.

According to Liebig, blood-fibrin is perfectly insoluble in *dilute hydrochloric acid*; he says that fibrin, macerated in water containing 10 per cent. hydrochloric acid, is gradually converted into a jelly, which shrinks on the addition of more concentrated acid, and again swells up with pure water, without, however, any appreciable quantity of fibrin being dissolved. Syntonin however dissolves in the dilute acid more or less completely, according to the source from which it has been obtained. Dumas and Cahours found that water containing 0.001 per cent. hydrochloric acid caused fibrin to swell, without, however, dissolving it after 48 hours' digestion. But the addition of a few drops of hydrochloric acid, or of rennet, rapidly effected its solution at 36° C. The experiments of Bouchardat seem the most reliable, and have since been confirmed by v. Baumhauer (Ann. Ch. Pharm. xlvii. 320); they prove that fibrin is not a homogeneous substance, but that it is composed of at least two bodies. When moist fibrin, prepared from whipped or coagulated blood, is steeped in water containing 0.0006 per cent. hydrochloric acid, and therefore scarcely acid to the taste or to litmus, it immediately swells up and is converted into a mass of very bulky flakes. The swollen vesicles are rent by prolonged maceration, and the greater part of the fibrin dissolves; always leaving, however, a certain portion insoluble in excess of the acidulated water. The soluble portion (albuminose) scarcely reddens litmus, rotates the plane of polarisation to the left, is precipitated in light flakes by heat, and yields a precipitate with excess of hydrochloric or nitric acid, with tannin, mercuric chloride, ferrocyanide of potassium, and possesses generally all the characteristics of egg-albumin (Gerh. iv. 466). The precipitate produced by carbonate of ammonia in the solution has the following composition (it left no ash on incineration):

		v. Baumhauer.	Verdell.
C	. . . .	52.9	
H	. . . .	6.9	
N	. . . .	15.9	
S	. . . .		1.6
O	. . . .		

Bouchardat terms the undissolved portion *epidermose*, and considers it to be identical with the chief constituent of the epidermis and of horny substances.

5. *Nitric acid* turns fibrin yellow, and readily dissolves it by ebullition, forming an orange-yellow acid substance, xanthoproteic acid. (Mulder.)

6. Concentrated *sulphuric acid* causes fibrin to swell, and dissolves it by heat. The dilute acid does not dissolve fibrin.

7. Glacial *acetic acid* dissolves the granulation of fibrin, without attacking the fibrous portions (Lebonte and Goumoens). Concentrated acetic acid immediately converts fibrin into a colourless jelly, dissolving readily in hot water (according to F. Simon, the gelatinous mass does not dissolve). The acetic acid solution, evaporated at a gentle heat, becomes covered with a film, and then assumes a gelatinous appearance; the dry residue is insoluble in water. The solution is precipitated by sulphuric and hydrochloric acids; also by alkalis, but the precipitate redissolves in excess of the precipitant.

8. *Tribasic phosphoric acid* renders fibrin gelatinous; the jelly dissolves in water and is not precipitated by excess of acid. *Metaphosphoric acid* behaves like sulphuric acid.

9. According to Lehmann and Zimmermann, the several kinds of fibrin dissolve, for the most part, in *alkaline salts*; syntonin, however, is insoluble in dilute nitre solution (Lehmann). Neither arterial nor venous fibrin, when boiled in water or exposed to the air for some time, is soluble in nitrate of potassium. (Denis, Scheerer.)

10. Denis employs the following process for dissolving fibrin in *nitrate of potassium*:—50 pts. well-washed moist venous fibrin are triturated with  $\frac{1}{2}$  of their weight of nitre; water equal to 4 times the weight of the fibrin employed is gradually added; and then  $\frac{1}{16}$  pt. of caustic soda or potash. The whole is allowed to digest at about 37° C., with constant agitation. The mixture first becomes gelatinous, then viscid, and, after a few days, liquid; a small residue always remaining. The liquid thus obtained coagulates by boiling, like albumin, and is precipitated by alcohol, mercuric chloride, acetate of lead, &c. If alkali be not added, the solution is precipitated by the addition of a large quantity of water (Gerh. iv. 468). The solution, exposed for some time to the air, gradually becomes turbid, and deposits flakes which are insoluble in the mother-liquor.

11. If fibrin be dissolved in potash, and acetic or phosphoric acid added to the solution till the precipitate first formed redissolves, a liquid is obtained, from which white flakes are precipitated by neutral salts (Panum). The potash-solution is precipitated by *mercuric chloride, sulphate of copper, and acetate of lead*.

12. *Tannin* of gall-nuts precipitates fibrin from its saturated solutions; it combines with moist fibrin, forming a hard imputrescible mass.

13. *Ferrocyanide of potassium* produces with the acetic acid solution a white precipitate, which at first redissolves but afterwards becomes permanent. It is not dissolved by diluted acids, but is decomposed by alkalis and even by ammonia.

14. *Sulphuric acid* with *peroxide of manganese, or acid chromate of potassium*, yields with fibrin the same products as with albumin (i. 67).

*Sources and physiological relations of Fibrin.*—Lehmann (*Gmelin's Handbuch*, viii. [2] 167), considers that fibrin is formed from albumin in the animal organism, possibly by the latter taking up oxygen, a mode of formation rendered highly probable by the results obtained by Snee (p. 639), in the artificial production of fibrin from albumin. The occurrence of fibrin in the chyle is not opposed to this view, partly because fibrin may be conveyed to this fluid by the lymphatics and blood-vessels, and partly because all the juices of the animal body contain free oxygen (Lehmann). Neither is the formation of fibrin from albumin by oxidation contradicted by the fact that in pneumonia, when a portion of the lung is rendered impermeable to air, and consequently the supply of oxygen must be diminished, the quantity of fibrin in the blood is increased. The fact is, that the conversion of albumin into fibrin is only the first stage in the process of oxidation, which, when further continued, transforms the fibrin into urea, and various other oxidised products, which pass into the excretions, so that the scanty supply of oxygen which the blood receives in certain diseases, may be sufficient to convert the albumin into fibrin, but not to oxidise it further.

Fibrin is not simply suspended in the blood, as Hunter and others supposed. It is not true that it is kept in solution by alkalis or alkaline salts, and that the coagulation is caused by the neutralisation of the solvent with carbonic acid from the air, since blood saturated with carbonic acid is found to coagulate much more slowly than blood deficient in the gas, and the addition of alkaline carbonates retards or entirely prevents the coagulation of blood. The cause of spontaneous coagulation is not known. Blood stagnated in veins, and thus shut out from the air, is always much longer in coagulating than when there is a free access of air. Hence the presence of air seems necessary for the coagulation of blood, as is rendered highly probable by numerous experiments, from which it has also been concluded, by trying the action of different gases, that oxygen is the principal, if not the sole agent. The coagulation of blood in closed vessels is probably due to the slow evolution of oxygen dissolved in the fluid of the blood-cells, and the rapid coagulation of blood in an exhausted receiver may arise from the sudden and rapid evolution of the gas. (*Gmelin's Handbuch*, viii. [2] 155-7.)

C. Schmidt thinks that, in the circulation, the fibrin is combined with neutral albuminate of sodium, forming an acid salt, which is resolved into its components on leaving the circulation. The fibrin forms the clot, while the albumin, which is precipitated from the serum on boiling, he supposes to have been previously in combination with chloride of sodium, which remains in the mother-liquor, together with the neutral albuminate. (*Gmelin's Handbuch*, viii. [2] 155.)

According to W. B. Richardson, the coagulation of fibrin is consequent upon an exhalation of ammonia from the blood; but this seems very doubtful. According to Lister (*Proc. Roy. Soc.* xii. 580), the coagulation is brought about catalytically by contact with foreign matter: whence blood remains fluid in the vessels, not because their walls exert any influence opposing coagulation, but because during life, and for some time after death, they do not act as exciters of coagulation.

It has been supposed that blood coagulates more slowly the less fibrin it contains; but this in many instances is not the case, and the coagulation of blood appears to be modified by other causes.—The blood of amphibious animals coagulates the most slowly, that of birds the most rapidly. The blood of the small veins contains more fibrin than that of arterial blood, in the proportion of 6 : 4, so that a considerable quantity of fibrin appears to be formed in the capillaries, although it must be remembered that the fibrin, owing to the diminution of blood-cells, is in part only relatively increased. The percentage of fibrin in the blood of the *vena cava* is, even when this blood is unmixed with the liver-blood (which does not contain fibrin), very small in proportion to that of arterial blood,—about 214 : 410. In accordance with these data, Lehmann considers that fibrin is principally formed in the arteries, increased in the capillaries, and disappears in the larger veins (*loc. cit.* p. 699).

Normal human blood contains about 2.55 per cent. fibrin (Nasse). Blood is said to yield less fibrin by agitation than by spontaneous coagulation, to the amount of 1/10 less (Marchal de Calvi). Abbeille, however, says that more fibrin is obtained from



blood by agitation than by spontaneous coagulation, and that blood heated to 60° C. yields by agitation more fibrin than at the common temperature, but that agitation has a greater effect on the quantity of fibrin than the temperature; blood coagulated at 0° C., yields less fibrin than at the common temperature. It was found that the blood of rabbits did not coagulate when carbonate of sodium or of potassium had previously been injected into the vein.

Coagulating blood cools much more slowly than non-coagulating blood at the same temperature. The passage of fibrin from the soluble to the insoluble state is either the cause of the evolution of heat, or hinders the process of cooling (Lehmann). According to Nasse and Poggiale, the blood of new-born children contains much less fibrin than that of adults, the augmentation being especially large at the age of puberty. According to Nasse, the blood of women contains on the average 2·20 per cent. of fibrin; according to Andral and Gavarret, the proportion increases during pregnancy, especially in the last three months. Lehmann found more fibrin in his own blood when living exclusively on animal diet, than on vegetable diet, a result which Nasse had arrived at by experimenting upon dogs (*Gmelin's Handbuch*, viii. [2] 188). The quantity increases by fasting or by blood-letting, while the number of blood-cells decreases.

The fibrin of portal blood is described by Schmidt as a viscid, gelatinous mass. That of *chyle* is distinguished from blood-fibrin by a lower degree of contractility and by not gelatinising. Like the fibrin of many morbid secretions, and that of fish, it sometimes, and especially in warm atmospheres, redissolves a few hours after coagulation. *Lymph-fibrin* is exactly like that of blood. Gorup-Besanez (*Ann. Ch. Pharm.* xciv. 166-9) found a peculiar kind of fibrin in an infiltrated liquid obtained from the chest of a tuberculous patient. It swelled up in water, and then formed a turbid solution on being heated. The residue from the evaporated solution dissolved readily by a gentle heat in hydrochloric acid of 1 per cent., but was insoluble in a solution of nitre containing 6 per cent. of the salt. Fibrin is not generally found in normal infiltrations.

The following table contains the percentages of fibrin in the blood of different animals:

	Nasse.	Poggiale.	Andral, Gavarret, and Delafond (average).
Ox . . . .	3·6 — 4·0	5·0	3·6
Cow . . . .			3·8
Sheep . . . .	3·0 — 3·8	3·2	3·2
Goat . . . .	3·35 — 3·9		3·15
Horse . . . .	2·4 — 2·85		4·0
Pig . . . .	3·6 — 3·9		4·6
Dog . . . .	1·7 — 1·9	2·2	2·1
Fowl . . . .	5·85	5·0	
Goose . . . .	3·4		
Pigeon . . . .		5·0	

(*Gmelin's Handbuch*, viii. [2] 188.)

Fibrin is dissolved by bile free from mucus. (Hünefeld.)

Fibrin is more easily digested than coagulated albumin or casein. With dogs it appears to digest entirely in the course of three hours. Its digestibility, however, is naturally influenced by the state of aggregation; boiled fibrin is more slowly digested than raw fibrin.

Mulder (*Jahresb. d. Chem.* 1859, p. 538) remarked that fibrin placed in a full bottle, with a little diastase, swelled up and partly dissolved, but after a time resumed its primitive form. He thinks this is owing to the fact that a given quantity of diastase can only effect the solution of one and the same quantity of fibrin, which, after the diastase has performed its office, again returns to its former state.

Fibrinous casts of the uriniferous tubes of the kidney are sometimes met with in the *urine* of persons suffering from Bright's disease; moreover the so-called *chylous urine* is sometimes spontaneously coagulable, from the solidification of fibrin.

Fibrin occurs in *milk* only when the latter contains blood.

In inflammatory diseases of the mucous membranes (*Diphtheria*, *Pneumonia*, *Dysentery*, *Bright's disease*, &c.), fibrin is found in the secreted mucus. C. E. L.

**FIBRIN, VEGETABLE.** *Insoluble vegetable albumin* (Berzelius). *Zymome* (Taddei).—The portion of the gluten of cereal plants, which is insoluble in alcohol; in the gluten of wheat it is mixed with gliadin; in that of rye and barley, also of buckwheat, with fatty and resinous substances.

To prepare it, wheat-gluten is repeatedly boiled with alcohol, till the liquid no longer leaves any residue on evaporation. It then remains in the form of a greyish-white,

elastic mass, still contaminated with small quantities of starch and chaff, from which it may be freed by solution in dilute potash, and precipitation with acetic acid; also with fat, which may be removed by subsequent treatment with ether. The gluten, after exhaustion with alcohol, may also be dissolved in very dilute hydrochloric acid, which easily takes up the fibrin, and yields it as a precipitate on neutralisation with ammonia. The hydrochloric acid solution behaves just like that of muscle-fibrin, and is precipitated in thick flakes by chloride of sodium.

Vegetable fibrin, when dry, forms a brownish horny mass, which recovers its former character by maceration in cold water. It dissolves in *acetic, hydrochloric, and phosphoric acids*, in the *fixed alkalis*, and in *ammonia*, and is precipitated from these solutions on neutralisation.

100 pts. of vegetable fibrin yield by analysis:

	Scherer.*		Jones.†	Dumas and Cahours.‡		Verdeil.§
	a	b	c	d	e	f
Carbon	54.2	54.2	53.1	53.2	53.4	53.7
Hydrogen	7.3	7.5	7.0	7.0	7.0	7.1
Nitrogen	15.8	15.8	15.6	16.4	16.0	15.8
Sulphur	.	.	.	.	.	.
Oxygen	.	.	.	.	.	1.0

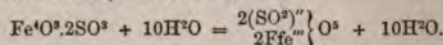
*a, c, d, e, f* were extracted from gluten of wheat; *b* from gluten of rye, *d* and *e* had been treated with diastase; *f* was the same as *e*, but had been kept in boiling water for three days, then washed and dried at 140° C.; *g* was extracted from rye.

These analyses show that vegetable fibrin has essentially the same composition as animal fibrin. The ash does not contain any soluble alkalis. (Liebig.)

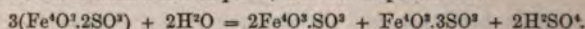
Vegetable fibrin undergoes gradual alteration in contact with moisture, and is transformed in a similar manner during the germination of cereal grains, giving rise in the latter case to the peculiar ferment called diastase (p. 319).

The green deposit which separates from expressed vegetable juices on standing, probably contains vegetable fibrin, but it has not been examined.

**FIBROFERRITE.** A basic ferric sulphate occurring in Chile in botryoidal masses, having a radio-fibrous structure and pale golden green colour. According to an analysis by F. Field (Chem. Soc. Qu. J. xiv. 156), it contains 31.94 per cent.  $\text{SO}^3$  31.89  $\text{Fe}^4\text{O}^3$ , and 35.90 water, whence the formula:



When exposed to the air for some weeks, it gives off 2 at. water; at the heat of the water-bath 7 at., and the remaining 3 at. at 250° C., leaving the anhydrous salt  $\text{Fe}^4\text{O}^3.2\text{SO}^3$ . It dissolves partially in cold water, imparting a slight acid reaction. In water of 43° C., it is resolved into an insoluble yellow ochrey substance =  $2\text{Fe}^4\text{O}^3.\text{SO}^3 + 3\text{H}^2\text{O}$ , soluble neutral ferric sulphate, and free sulphuric acid:



The insoluble ochrey substance is often found associated with fibroferrite. (Field.)

**FIBROÏN.** A substance allied in composition to horny tissue, and constituting, according to Mulder (Pogg. Ann. xxxvii. 294; xl. 266), the fibre of silk and of gossamer-threads. It is obtained pure by exhausting raw silk successively with boiling water, alcohol, ether, and acetic acid; these solvents removing albumin, a glutinous substance, fat, and colouring matter. The silk, after this treatment, is very white, soft to the touch, and destitute of lustre. It contains, after deduction of ash, 48.53 per cent. carbon, 6.50 hydrogen, 17.35 nitrogen, and perhaps a little sulphur, besides oxygen. The ash, which is in considerable quantity, contains lime, magnesia, ferric oxide, oxide of manganese, and soda, in combination with carbonic, sulphuric, hydrochloric, phosphoric, and silicic acids.

Fibroin, when calcined, emits the odour of burnt horn. By dry distillation, it yields a large quantity of carbonate of ammonia, water, empyreumatic oil, and an abundant residue of charcoal. Dilute aqueous *potash* does not act upon it in the cold, but dissolves it at the boiling heat. Strong potash-ley dissolves it, forming a solution which is precipitated by acids and even by pure water. Solid hydrate of potassium converts it into oxalate. Fibroin does not dissolve in *ammonia* or in *alkaline carbonates*. Strong *sulphuric acid* dissolves it in the cold, forming a thick liquid, which forms with water a solution precipitable by infusion of gall-nuts and by caustic potash; the precipitate formed by potash dissolves, however, in excess of the reagent. Strong

\* Ann. Ch. Pharm. xl. 1.  
† Ann. Ch. Phys. [3] vi. 485.

‡ Ibid. xl. 67.  
§ Ann. Ch. Pharm. lvi. 317.

*hydrochloric acid* dissolves fibroin, the solution turning brown when heated. Dry fibroin absorbs 7.4 per cent. hydrochloric acid gas. Fibroin likewise dissolves in strong *nitric acid*, yielding oxalic acid when heated, and in *phosphoric acid*.

The organic matter of sponges exhibits the same characters as the fibroin of silk; after exhaustion with dilute hydrochloric acid, alcohol, and ether, and drying at 100° C., it contains:

C	H	N	S	P	I	O	
46.51	6.31	16.15	0.50	1.90	1.08	27.55	Crookewit (Ann.Ch. Pharm. xlviii. 43).
48.50	6.29	16.15	ash	3.59			Posselt ( <i>ibid.</i> xlv. 192).

According to Mulder, the organic matter of sponges is a combination of fibroin with sulphur, phosphorus, and iodine; but these elements, with the exception of sulphur, do not form an essential part of the organic matter. (Gerh. iv. 499.) See SPONGE.

**FIBROLITE.** A fibrous variety of **SILLIMANITE** (*q. v.*)

**FICHTELITE.** A fossil resin, isomeric with oil of turpentine, found together with kőnlite, at Redwitz in the Fichtelgebirg. It forms small monoclinic crystals, melts at 46° C., and solidifies at 36° in the crystalline state. Slightly soluble in alcohol, easily in ether, and separates therefrom in tabular crystals, exhibiting the combination  $\text{oP} : +\text{P} : -\text{P} : -\text{P}\infty : +\text{P}\infty$ , but with the pair of faces  $-\text{P}$  wanting on the right of the orthodiagonal, and the pair  $+\text{P}$  on the left. Inclination of  $\text{oP} : -\text{P}\infty = 127^\circ 45'$ ;  $\text{oP} : +\text{P}\infty = 106^\circ 25'$ ;  $-\text{P} : -\text{P}$  (on the orthodiagonal)  $= 99^\circ 0'$ ;  $+\text{P} : +\text{P}$  (on the same axis)  $= 108^\circ 40'$ ;  $-\text{P}\infty : +\text{P}\infty$  (at the base)  $= 125^\circ 50'$  (Clark, Ann. Ch. Pharm. cxix. 226). Schrötter (Pogg. Ann. lix. 37), by exhausting the pine-wood found at Redwitz, which is impregnated with fossil resin, with ether, obtained xyloretin (*q. v.*), which crystallised from the solution, and an oily mass which deposited a small quantity of brown resin, and then a light yellow liquid, smelling like benzoin, sparingly soluble in alcohol, easily in ether, and having the same composition as fichtelite; it may be called liquid fichtelite. Analysis gave:

	Solid Fichtelite.		Liquid Fichtelite.
	Bromels.	Clark.	Schrötter.
Carbon	88.07	87.13	88.58
Hydrogen	10.70	12.87	11.34
	98.77	100.00	99.92

Both these substances, as well as hartite and tekoretin, have the composition  $\text{C}^{10}\text{H}^{14}$ . (Rammelsberg's Mineralchemie, p. 976.)

**FICARIA.** The plant called pile-wort (*Ranunculus Ficaria*, L. *Ficaria ranunculoides*, Dec.), is said, by St. Martin (Rép. Chim. app. i. 425), to contain a peculiar substance called ficarin, closely resembling saponin, and differing therefrom only in not being coloured by ferric chloride. It is said to be obtained by treating the aqueous extract with alcohol, or the alcoholic extract with water, and evaporating. The leaves give only traces of it, the tubers more, and the roots a still larger quantity.

The plant is also said to contain an acrid volatile acid, easily decomposed by heat, and probably occurring in all plants of the ranunculaceous order.

**FICARIN.** See **FICARIA**.

**FICINITE.** See **VIVIANITE**.

**FICUS.** The stems and branches of plants of this genus yield a viscid milky juice, containing caoutchouc or resinous substances resembling it: caoutchouc is most abundantly contained in the juice of the stem of *Ficus elastica*, from which a considerable portion of the caoutchouc of commerce is obtained.

The milky juice obtained from the young stems of the common fig-tree (*Ficus carica*) has an aromatic odour, and sharply aromatic, bitter taste, reddens litmus slightly, does not coagulate when boiled, but deposits a white viscid substance. It contains an odoriferous substance, cerin, a very small quantity of a hard resin insoluble in ether, caoutchouc, a deliquescent extractive matter having a sharp, bitter, nauseous taste; also gum, albumin, sulphates, chlorides, the salts of vegetable acids, and a free vegetable acid. (Geiger and Reimann.)

The juice which exudes from the milky husks of green figs contains cerin, a resin having a sharp burning taste, and a substance like caoutchouc. On exhausting the husks with alcohol, and distilling the alcoholic extract, an acrid distillate is obtained, which deposits crystals; the residue is a resin quite free from acidity (Landerer.) Dried figs contain, according to Bley, fat, sugar, extractive matter, chloride of calcium,



a salt of phosphoric acid, vegetable fibre, and (?) seed-germs. (*Rochleder's Phytochemie*, p. 203.)

The milky juice of the young branches of *Ficus elastica* contains viscain (a ductile, soft resin, insoluble in alcohol), resin, wax, gum, extractive matter, and a lime-salt. That of the stem is similarly constituted, but contains caoutchouc instead of viscain. (Nees v. Esenbeck and Clamor-Marquart.)

The fresh acid creamy juice of *Ficus sylvestris* (St. Hilaire), and *F. doliaria* (Mart), South American species, dries up in the sun to a reddish-yellow elastic mass, resembling gutta-percha, easily soluble in ether and chloroform, nearly insoluble in alcohol. The fresh juice, when filtered, leaves on the filter a white leathery mass, containing a substance resembling caoutchouc (amounting to 11.1 per cent. of the entire juice), an amorphous substance (5.2 per cent.), and a granular substance (0.47 per cent.) soluble only in hot alcohol and ether, a substance (1.15 per cent.) soluble in cold alcohol and ether, a resinous bitter substance (0.2 per cent.), and a waxy substance (0.3 per cent.) The filtered light brownish liquid contains 4 per cent. of a substance resembling uncrystallisable sugar, and a gummy substance soluble in water (together with the salts of an organic acid, albumin, tannin, and a small quantity of a free organic acid, in all 17.0 per cent.). Peckolt (*Arch. Pharm.* [2] cv. 31; *Jahresber. d. Chem.* 1861, p. 743).

*Ficus rubiginosa*, an Australian species, yields a resinous exudation, resembling euphorbium in appearance, varying in colour from dirty yellow or red to almost white, solid, generally brittle, but tough in the interior of large pieces, opaque, with dull and wax-like fracture; at 30° C., it softens and becomes plastic, like gutta-percha, but not sticky, provided it has been previously wetted with water. In its natural state, it has neither taste nor odour, but evolves an odour like that of wax when heated, and evinces a characteristic taste on being masticated. It is quite insoluble in water, either hot or cold. The greater part of it is soluble in cold alcohol, and a considerable portion of the remainder in hot alcohol, and by treating it with these solvents in succession, it may be separated into the following constituents:

Resinous substance, Sycoretin, easily soluble in cold alcohol	73
White crystalline substances, chiefly Acetate of sycoceryl, $C^{25}H^{40}O.C^2H^3O$ , insoluble in cold but soluble in warm alcohol	14
Caoutchouc, fragments of bark, sand, and loss	13

Warren de la Rue and Hugo Müller (*Chem. Soc. J.* xv. 62). See SYCOCERYL and SYCORETIN.

**FIELDITE.** A massive mineral, resembling grey antimonial copper, from the neighbourhood of Coquimbo in Chile, soft and unctuous to the touch, with dark greenish-grey colour, and red streak. An analysis by Field (*Chem. Soc. Qu. J.* iv. 332), gave:

S	Sb	As	Cu	Zn	Fe	Ag
30.35	20.28	3.91	36.72	7.26	1.23	0.07 = 99.82;

whence Rammelsberg (*Mineralchemie*, p. 993) deduces the formula  $4M^S.Sb^S.S^3$  or  $M^S.2M^S.Sb^S$ , the antimony being partly replaced by arsenic, and the symbol M standing for Cu, Zn, and Fe.

**FIGURE STONE.** See AGALMATOLITE (i. 60).

**FILICIC ACID.**  $C^{15}H^{16}O^3$  or  $C^{26}H^{16}O^{10}$ ? (Luck, *Jahrb. pr. Pharm.* xxii. 129; *Jahresber. d. Chem.* 1861, p. 558.)—An acid obtained from the root of the common male fern, *Aspidium Filix mas*. The extract of the root (especially of that collected in autumn), prepared with anhydrous ether, and concentrated to an oily consistence, deposits the acid after a few days in the form of a greenish-yellow powder, or a yellow crust, which may be purified by washing with a mixture of alcohol and ether, and recrystallisation from ether; or the impure filicic acid, after washing with ether-alcohol and pressing, may be suspended in warm alcohol, and dissolved by addition of a little ammonia, the solution filtered, the filtrate being allowed to drop into dilute hydrochloric acid, and the washed precipitate treated with warm alcohol of 80 per cent., till it no longer colours the alcohol.

Filicic acid thus prepared is a whitish-yellow or light yellow crystalline powder, insoluble in water, weak alcohol, and acetic acid; sparingly soluble in strong alcohol, more soluble in ether (especially in presence of a small quantity of fixed oil): the solution reddens litmus. It dissolves also in fixed oils, oil of turpentine and rock-oil, and very easily in sulphide of carbon. It melts at 161° C., and solidifies in the amorphous state; decomposes at a higher temperature. Luck expresses its composition by the improbable formula  $C^{26}H^{16}O^9$ .

Filicic acid dissolves readily in alkalis. The *sodium-salt* forms an amorphous gummy mass, whose solution yields with neutral acetate of lead, a yellowish-white curdy precipitate, which, when dried in vacuo (as were also the following substances), has, according to Luck, the composition  $PbO.C^{22}H^{14}O^{10}$ ; it should perhaps be  $C^{22}H^{14}PbO^{10}$ , or  $C^{12}H^{14}PbO^4$ .

*Chlorofilicic acid*,  $C^{12}H^{12}ClO^4$ , or  $C^{22}H^{12}ClO^{10}$  (?), produced, with evolution of hydrochloric acid, by the action of chlorine gas on solid filicic acid, is a turpentine-like mass, which, after solution in alcohol and spontaneous evaporation, separates in yellow-brown amorphous drops. The alcoholic solution forms with acetate of lead, a loam-coloured precipitate, which contains  $PbO.C^{22}H^{12}ClO^{10}$ , according to Luck; more probably  $C^{12}H^{12}PbClO^4$ . When treated with strong alcohol, it gives up part of its acid. *Trichlorofilicic acid*,  $C^{12}H^{12}Cl_3O^4$ , or  $C^{22}H^{12}Cl_3O^{10}$  (?), is obtained by the action of chlorine on filicic acid suspended in water, as a yellow powder insoluble in cold water, but soluble in hot water, and in alcohol, ether, and oils, both fixed and volatile. Its alcoholic solution forms with acetate of lead, a loam-coloured precipitate containing  $PbO.C^{22}H^{12}Cl_3O^{10}$  (Luck), more probably  $C^{12}H^{12}PbCl_3O^4$ .

**FILIMELISIC ACID.** See FILIPELOSIC ACID.

**FILIMELISI-SULPHURIC ACID.** Filicic acid dissolves without decomposition in cold sulphuric acid of ordinary strength, but by triturating it with fuming sulphuric acid, a solution is formed which, when dropped after a few hours into a dilute solution of sulphate of sodium, yields a precipitate of filimelisi-sulphuric acid; this, when purified, forms a golden-yellow powder, somewhat soluble in water, more soluble in alcohol and ether. Its *barium-salt* is amorphous, of red-lead colour, soluble in water. The formation of the acid as above described, is attended with that of butyric acid. Luck (*loc. cit.*) assigns to the acid the formula  $C^{22}H^{12}O^4.SO^2$ , and to the barium-salt,  $BaO.C^{22}H^{12}O^4.SO^2$ , both of which are improbable.

**FILIPELOSIC ACID.**  $C^{12}H^{12}O^4$ , or  $C^{22}H^{12}O^8$  (?) (Luck, *loc. cit.*).—Obtained by dissolving filicic acid in warm, very dilute potash-ley, exposing the solution to the air for a week, and precipitating the filtrate with dilute sulphuric acid; purified by washing, drying, solution in ether-alcohol, and spontaneous evaporation. When filicic acid is heated for some time with dilute alcoholic ammonia to  $80^\circ$  or  $100^\circ$  C. out of contact with the air, the liquid then precipitated by dilute sulphuric acid, and the precipitate purified as above, Luck's filimelisi acid is obtained.

The product obtained by the first method, is an amorphous loam-coloured powder; the second yields an ochre-coloured powder, composed of microscopic spherules. Both are tasteless, insoluble in water, soluble in alcohol, ether, oils both fixed and volatile, and sulphide of carbon.

Luck regards the two products thus obtained as different, assigning to the former (his *filipelosic acid*) the formula  $C^{22}H^{12}O^8$ , and to the latter (his *filimelisi acid*), the formula  $C^{12}H^{12}O^4$ , though they agree in their properties, and in the composition of their lead-salts, that of the former yielding 31.96 per cent. lead-oxide, and that of the latter 32.62 per cent.; the formula  $C^{12}H^{12}PbO^4.H_2O$  requires 33.7 per cent. lead-oxide.

*Chlorofilipelosic acid*,  $2C^{12}H^{12}ClO^4 + H_2O$  (?), is a light brown amorphous substance formed by the action of chlorine on dry filipelosic acid; and *Dichlorofilipelosic acid*,  $C^{12}H^{12}Cl_2O^4$  (?), produced by the action of chlorine on filipelosic acid suspended in water, is a loam-coloured powder, whose lead-salt appears to contain  $PbHO.C^{12}H^{12}PbCl_2O^4 + \frac{1}{2}$  aq. (?) (Luck, *loc. cit.*)

**FILIXOLINIC and FILOSMYLIC ACIDS.** When a recently prepared ethereal extract of the root of *Filix mas* is diluted with a little ether and alcohol, and then shaken up with twice its volume of water and a little ammonia, two layers are formed after a while; the lower of which is brown, and is said to contain filicic or filimelisi acid, while the upper, which is dark green and oily, yields a transparent oil, green by reflected, colombo-red by transmitted candle-light, and remaining liquid even at very low temperatures. This oil is said to yield by saponification a non-volatile acid, filixolinic acid,  $C^{22}H^{12}O^4$  (*barium-salt*,  $BaO.C^{22}H^{12}O^4$ ), and after saponification a volatile acid, filosmylic acid, whose *barium-salt* contains  $BaO.C^{22}H^{12}O^4$ . (Luck, *loc. cit.*) These, like the formulæ assigned by Luck to most of the preceding compounds, are very improbable.

**FILIX.** The root of *Aspidium Filix femina* (A), and of *Aspidium Filix mas* (B), also the frond of the latter (C), all in the dried state, have been analysed by H. Bock (Arch. Pharm. [2] lxx. 257; Jahresber. d. Chem. 1851, p. 557). The results are given in the following table:

	A.	B.	C.
Volatile oil . . . . .	0.02	0.04	trace
Fixed oil . . . . .	1.2	6.0	
Stearin . . . . .	. .	1.0	
Resin . . . . .	0.4	4.0	
Wax . . . . .	. .	. .	0.5
Vegetable gelatin . . . . .	1.3	0.4	
Gum . . . . .	2.0	3.3	
Albumin . . . . .	5.0	3.5	5.4
Mucus . . . . .	. .	. .	5.7
Starch . . . . .	7.5	10.0	
Sugar . . . . .	. .	11.0	
Pectin . . . . .	4.0	2.1	3.5
Chlorophyll . . . . .	. .	. .	8.7
Tannic and gallic acids . . . . .	11.9	10.0	11.0
Fibre containing starch . . . . .	1.5	1.5	
Ash . . . . .	4.94	2.1	5.0
Woody fibre and loss. . . . .	60.24	45.06	60.2
	100.00	100.00	100.0

The ash contains :

Silica . . . . .	0.2	0.01	0.2
Sand. . . . .	0.9		
Sulphate of calcium . . . . .	0.3	0.11	0.3
Ferric phosphate . . . . .	0.08	trace	0.1
Phosphate of calcium . . . . .	0.1	0.16	0.4
Phosphate of magnesium . . . . .	. .	0.04	
Carbonate of calcium . . . . .	1.2	0.94	1.3
Chloride of sodium . . . . .	0.1	0.04	0.3
Chloride of potassium . . . . .	0.4	0.22	0.6
Carbonate of potassium . . . . .	1.3	0.55	1.5
Loss . . . . .	0.36	0.03	0.3
	4.94	2.10	5.0

The granular deposit which gradually settles down from the ethereal extract of the root of *Aspidium Filix mas*, and was formerly observed by Trommsdorff and Osann, is regarded by Bock as the more solid portion of the fixed oil. According to Luck, it consists chiefly of filicic acid (ii. 646).

The decoction obtained by boiling fern-roots with alcohol yields, on addition of water, a little hydrochloric acid, and sulphate of sodium, a precipitate containing two tannic acids, viz. pteritannic and tannaspidic acids (*q. v.*)

**FILTRATION.** The separation of a liquid from solid matter suspended in it by passing through a porous substance which retains the suspended matter, but allows the liquid to pass through. Various materials are used for this purpose, according to the nature of the liquid to be filtered; viz. paper, linen, calico, woollen cloth, sand fine and coarse, pounded glass, charcoal, &c.; but for analytical operations, and for most laboratory preparations, the material used is unsized paper. For straining viscid liquids, such as syrups and white of egg, which will not readily pass through paper, cloth filters are used; and corrosive liquids, such as strong acids and caustic alkaline solutions, may be filtered through pounded glass.

Paper for filtration must be sufficiently porous to allow liquids to pass through it quickly. The degree of porosity required varies of course with the particular purpose to which the paper is to be applied: for analytical operations, it must be sufficiently close-grained to arrest the passage even of very fine solid particles. In some manufacturing, the requisite degree of porosity is given to the paper, by leaving the wet sheets to freeze at a winter temperature; the expansion of the water in freezing, separates the fibres of the paper from one another, and gives it a regular porosity which cannot be attained by any other method. Paper which filters slowly may be improved in quality by this treatment.

All paper contains a certain quantity of inorganic material, and mostly leaves, when incinerated, a quantity of ash sufficient to induce appreciable error in analytical operations. Hence it is necessary, either to remove the inorganic matter by digesting the filters in dilute nitric acid, and afterwards washing them thoroughly with distilled water, which is a tedious and troublesome operation — or else to determine the quantity of ash left by the filter and allow for it. For this purpose, ten or twelve filters of each size used in the laboratory for analytical purposes, should be burnt, the ash of each



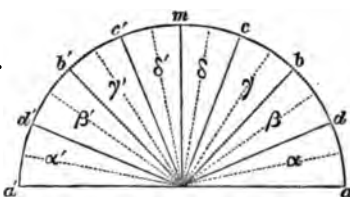
lot weighed, the quantity of ash left by an individual filter thence calculated, and a record kept of the results.

All this trouble may, however, be saved, and analytical operations greatly facilitated, by using the Swedish filtering paper, which is prepared at Fahlun and Lessebo, with a spring-water nearly as pure as distilled water. This paper, besides having the property of filtering very quickly, being prepared in winter as above mentioned, is singularly free from inorganic matter, giving up scarcely anything to dilute acids, and leaving when incinerated only 0.2 per cent. ash. A sample of this ash analysed by Plantamour yielded 63.23 per cent. silica; 12.83 lime; 6.21 magnesia; 2.94 alumina; and 13.92 ferric oxide.

Paper filters are of two forms, plain and folded. They are sold ready cut in circles of various sizes. To make a plain filter, it is only necessary to fold the paper twice, so as to give it the form of a quadrant; and this when half opened, forms a cone whose edges meet at an angle of  $60^\circ$ ; the funnel on which the filter is laid, should therefore also have its sides inclined at  $60^\circ$ . For collecting precipitates which are to be afterwards removed from the filter by washing or otherwise, the plain filter is decidedly the best form; but when the precipitate is only a refuse product, or need not be very carefully removed from the filter, and the principal object is to filter quickly, folded filters are to be preferred, because the folds leave channels between the paper and the surface of the funnel, which facilitate the passage of the liquid.

The following method of making a folded filter is given by Mohr (*Lehrbuch der pharmaceutischen Technik*, p. 217). The circular filter is first folded in halves along the line  $a a'$  (fig. 479), and then in quarters, making the fold  $m$ . The filter is then again half opened, as in the figure, and  $a$  is laid on  $m$ , forming the fold  $b$ , also  $a'$  on  $m$ , forming  $b'$ . Next  $a$  is laid on  $b'$ , forming  $c$ , and  $a'$  on  $b$ , forming  $c'$ ; then  $a$  is laid on  $b$ , forming  $d$ , and  $a'$  on  $b'$ , forming  $d'$ . All the folds thus produced are turned the same way, namely, with their concavities upwards. The next thing to be done is to make folds between each of these turned the contrary way.

Fig. 479.



For this purpose,  $a$  is first laid on  $b$  in the fold  $d$ , and then turned back to  $d$ , making the fold  $a$ ; then  $a d$ , as they lie together, are turned over to  $c$  and folded back to  $b$ , making  $\beta$ ;  $a d b$  is laid on  $m$  in the fold  $b$  and turned back to  $c$ , making  $\gamma$ ; and lastly,  $a d b c$  is laid on  $c'$  and turned back to  $m$ , making  $\delta$ . Corresponding folds are then made on the other side, viz. by laying  $a'$  on  $b'$  and turning it back to  $d'$ , then  $a' d'$  on  $c'$  and back to  $b'$ ; then  $a' d' b'$  on  $m$  and back to  $c'$ , and  $a' d' b' c'$  on  $c$  and back to  $m$ . If the filter be now opened, all the folds will be found directed alternately outwards and inwards, excepting  $a$  on the one side, and  $a'$  on the other; all four of which have their convexities outwards. Intermediate folds turned inwards must therefore be made halfway, between  $a$  and  $a'$ , and between  $a'$  and  $a$ ; and then all the alternate folds will be in contrary directions. The whole thing is much easier to do than to describe.

A folded filter of simpler construction, and containing a sufficient number of folds for most purposes, is made as follows. The circular disk of paper is first folded in halves and quarters as before. It is then half opened as in fig. 479;  $a$  is turned over to  $m$ , making the fold  $b$ , and  $a'$  to  $m$ , making  $b'$ ; then  $a$  is turned back to  $b$ , making  $d$ ,  $a'$  to  $b'$ , making  $d'$ ; lastly,  $a d b$  is turned backwards to  $m$ , making  $c$ , and  $a' d' b'$  also backwards to  $m$ , making  $c'$ . On opening the filter, all the folds are found to be alternate in direction excepting  $a$  and  $a'$ , between which intermediate folds are to be made as before. Folded filters fit best into funnels of about  $60^\circ$  aperture.

Before collecting a precipitate on a filter, the filter must be moistened all over with water or alcohol, as the case may be; otherwise the first portions of the precipitate are very apt to run through and render the filtrate turbid; it is also advisable to leave the precipitate to settle down in the precipitating vessel to a considerable extent, then to pass the clear liquid through the filter, and afterwards pour the precipitate upon it, (see DECONTANTION, p. 308). Most precipitates filter best after boiling. The size of the filter should be such as to leave at least half an inch of clear margin when the whole precipitate is collected upon it; otherwise, portions of the precipitate are very apt to creep over the edges during washing.

In washing precipitates for quantitative analysis, it is desirable to use as little water as possible, as the evaporation of wash-waters always takes a considerable time: care should therefore be taken, after adding each portion of water, to let the last drop run through before adding any more, and the wash-water must be tested from

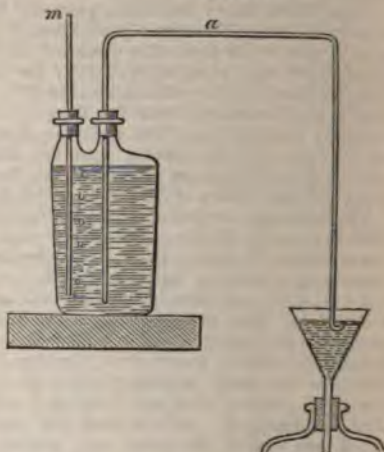
time to time by evaporating a drop of it on platinum-foil, the washing being continued till a drop thus evaporated leaves no residue. It must not be forgotten, however, that many precipitates are slightly soluble in water, and, therefore, the wash-water which runs from them will always leave a trifling residue. In such case, testing with reagents must be resorted to.

When the quantity of water used for washing is immaterial, as in most preparations, a continuous mode of washing may be adopted. There are many ways of effecting this. The simplest is to fill a flask with water and invert it with its mouth dipping

Fig. 480.



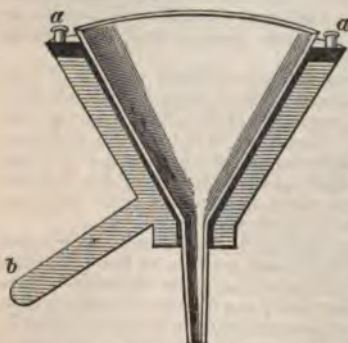
Fig. 481.



below the water in the filter, supporting it on a stand, as shown in *fig. 480*. As the liquid by filtration falls below the lip of the bottle, air will enter, and let down a fresh supply of water to feed the filter.

Another convenient apparatus for continuous washing is the siphon-bottle, shown in *fig. 481*. The bottom of the bottle is placed on a level with the surface of the water in the filter; air is blown in through the tube *m* till the siphon-tube *a* is filled with water; and *m* is then drawn up to such a height that air-bubbles may pass through it as the liquid sinks in the filter.

Fig. 482.



Liquids holding in solution substances which separate out on very slight reduction of temperature, often require to be filtered at the boiling heat. For this purpose the glass funnel containing the filter is placed within a double funnel (*fig. 482*), closed on all sides excepting at the apertures *a a*, one for pouring in water, the other for the escape of vapour, and having on one side a projecting tube closed at *b*, to which heat is applied by a spirit or gas-flame. The vessel is filled with water or oil according to the temperature required.

Water for economical purposes may be freed from turbidity by filtering through sand. A large earthen funnel, or stone bottle with the bottom beaten out, may have its neck loosely stopped with small stones, over which smaller stones may be placed, supporting layers of gravel increasing in fineness, and lastly covered to the depth of a few inches with fine sand, all thoroughly cleansed by washing. This apparatus is superior to a filtering stone, as it will cleanse water in large quantities, and may readily be renewed when the passage is obstructed, by taking out and washing the upper stratum of sand.

A similar method is used for filtration of water on the large scale. (See *Graham's Elements of Chemistry*, 2nd. ed. vol. i. p. 317; also the article FILTRATION in *Ure's*

*Dictionary of Arts, Manufactures, and Mines*, ii. 206, which likewise contains many useful details relating to filtering in manufacturing operations.)

**FIORITE.** *Pearl sinter.*—A variety of opal, occurring in the cavities of volcanic tufa, in smooth, shining, globular and botryoidal masses, having a pearly lustre.

**FIREBLANDE.** A mineral containing 62·3 per cent. silver, together with sulphur and antimony, found in the Kurprinz mine, near Freiberg, and at Andreasberg. Forms delicate monoclinic crystals grouped like stilbite. Hardness = 2, specific gravity = 4·2–4·3. Lustre pearly, adamantine. Colour hyacinth-red. Translucent. Sectile and somewhat brittle. (Dana, ii. 88.)

**FIRE-CLAY.** Fire-clays are hydrated silicates of alumina, capable of resisting exposure to high temperatures without melting or becoming in a sensible degree soft or pasty. They occur immediately below the several seams of coal in the carboniferous formation, and would appear, from the frequent remains of *Stigmaria* which they contain, to represent the soils of those luxuriant forests, which by heat and pressure have been converted into coal.

The plasticity of clays depends upon the combined water which they always contain, and which is expelled at a red heat. Hence, a clay once burned, recovers none of its plasticity when wetted.

The relation of the silica and alumina in fire-clays is very variable, as is also the amount of silica which exists in them in an uncombined condition, or as sand. Thus in five German clays examined by Dr. Percy, the total percentages of silica existing as sand, as hydrate, and in combination with bases, were as below:

	1	2	3	4	5
Silica as sand . . . .	56·95	47·40	16·20	29·63	18·29
„ as hydrate . . . .	1·39	1·06	1·05	·91	·98
„ combined with bases .	18·69	26·98	45·53	37·74	45·53
Total silica . . . .	77·03	75·44	62·78	68·28	64·80

The most celebrated and refractory fire-clays are those obtained at Stourbridge, in Worcestershire, and there extensively manufactured into furnace-bricks of all kinds, gas-retorts, glass-house pots, &c., the very finest and purest samples being alone devoted to this last application. The clay, as brought from the mine, is sorted into qualities (best, seconds, offal, &c.), according to its appearance and the size of the lumps, all such portions as exhibit streaks or spots of iron pyrites or other metallic substances, being rejected.

A pure silicate of alumina is the ideal type of a pure clay, and the nearest approach to this standard is presented by some of the French clays, of which analyses are given below. The impurities commonly present are oxides of iron, lime, magnesia, and the alkalis; frequently also small quantities of organic matter, the occurrence of which is usually unimportant, as it is burnt off in the process of firing.

The silicates of alumina are, as is well known, almost infusible, while the double silicates of alumina with other bases are readily melted at a comparatively low temperature. The importance of selecting clays free from these impurities is, therefore, obvious, since the fusibility of the substance increases directly with their amount; it is found in practice that 4 or at the most 5 per cent. is the maximum of oxides of iron, lime, magnesia, and alkalis together which can be present without rendering the mineral useless for its finer applications, while the samples most sought after contain not more than from 2 to 3 or 3½ per cent. of those bases. It is also found that the presence of a certain percentage of silica is essential to constitute a “strong” clay, while any considerable increase in the proportion of alumina tends to produce a “weak” clay, deficient in cohesion and unable to stand the severe tests to which it is subjected in the manufacture.

It may be here observed that the colour of a raw clay generally presents no indication whatever of its value, the variations in its shade being caused by minute quantities of organic matter. Neither does the colour of a burnt clay afford by any means an accurate criterion of its quality; for although the presence of a large quantity of iron is sufficiently palpable, the other and equally injurious impurities produce no effect upon its tint.

A firebrick or pot of good quality and properly burned, is nearly white, or of a pale cream or pinkish colour, free from black spots; the colour of a potsherd or fragment of a glass-house pot, after exposure to the intense heat of the furnace for many weeks, approaches to dark grey, or black, the fracture being almost vitreous, and the texture compact. A brick or pot which has been exposed, as, for instance, in the crown of a glass-house furnace, for a shorter time, presents, upon the face next to the fire, the



same appearance as a potsherd, gradually changing from the surface inwards, and being replaced first by a reddish colour, and finally by the original shade of the brick or pot.

It is probable that the first effect of heat is merely to peroxidise the iron, producing a red colour, while the application of a continued higher temperature produces a real combination, with a corresponding development of the grey or black colour of the silicate of aluminium and iron, and possibly a reduction of the iron to the state of magnetic oxide.

The drying and burning of the clay is attended with a considerable diminution of bulk, and it becomes a matter of much importance to reduce this shrinking to a minimum; a result effected by the admixture with the tempered clay of a certain quantity of calcined clay and potsherds ground to a coarse powder. The proportion of potsherds and calcined clay added to raw-clay varies much, according to the plasticity of the latter, and the judgment of the manufacturer. A proportion of  $\frac{1}{3}$  potsherds to the raw clay is adopted by many.

The importance of this admixture was well illustrated in a recent trial, in which the defendant alleged that the quality of clay supplied to him by the plaintiff was inferior, while the plaintiff affirmed that the destruction of the crown of the arches in defendant's glass furnaces was the natural consequence of his using an unusually and improperly small amount of potsherds, whereby the shrinking had been increased, and the fissures thus produced between the bricks had acted as *points d'appui* for the fire, at which fusion had taken place. The consequence was the production of droppings or "tears" of melted clay, which had fallen into the glass below and destroyed it in large quantities.

A brick manufactured from best Stourbridge clay, without admixture of potsherds, and 9 inches in length, contracted on burning  $\frac{1}{4}$  of an inch, and subsequently, after 21 days exposure to a white heat  $\frac{1}{10}$  more; a very fine clay from Tamworth (No. 9 in Table II.), rich in silica, contracted only  $\frac{2}{3}$  of an inch; while an inferior and highly aluminous clay, soapy to the touch and extremely plastic, shrank under like circumstances  $1\frac{1}{2}$  inch.

Tables I. and II. exhibit the composition of several fire-clays, British and foreign:

TABLE I.—Composition of Continental Fireclays.

	Forges des Eaux.	St. Amand.	Hessian crucibles.	Beau, Ardenne.	Dourdan, Seine-et- Oise.	Labou- chade, near Montluçon.	Savanas, Ardèche.
	Berthier.	Berthier.	Berthier.	Salvétat.	Salvétat.	Berthier.	Salvétat.
Silica . . . .	73	73.3	70.9	63.57	60.60	55.40	58.76
Alumina . . .	27	24.0	24.8	27.45	26.39	26.40	25.10
Sesquioxide iron	trace	2.7	3.8	1.5	2.50	4.20	2.50
Magnesia . . .	. .	. .	trace	trace	. .	. .	2.51
Lime . . . .	. .	. .	. .	.55	.84	. .	trace
Water, combined	. .	. .	. .	8.64	9.20	12.00	11.05
do. hygroscopic	. .	. .	. .	1.27	. .	. .	1.45

Riley (Chem. Soc. J. xii. 13; xv. 311) has shown that nearly all clays contain small quantities of titanium, which may be detected and estimated by treating the silica (separated in the usual way by fusion) with carbonate of soda, and with hydrofluoric acid containing a little sulphuric acid. The silicon is then volatilised as fluoride, while the titanium remains in the form of titanic anhydride,  $TiO_2$ . (For the details of the method, see SILICON AND TITANIUM.)

TABLE III.—Percentage of Silica and Titanic anhydride in several samples of Fire-brick.

	$SiO_2$	$TiO_2$
Stourbridge . . . . .	65.11	1.05
" . . . . .	63.42	1.05
Newcastle . . . . .	60.49	0.60
" . . . . .	60.60	0.42
" . . . . .	55.86	0.67
Wortley, Leeds . . . . .	62.96	0.96
Hawarden, North Wales . . . . .	62.39	0.69
Yellow London Clay . . . . .	64.52	0.50
Ewell brick, Surrey . . . . .	91.84	trace
Dinas brick, South Wales . . . . .	94.33	trace
Black Alder, Devonshire . . . . .	75.16	trace

TABLE II.—Composition of various English Fireclays, as compared with ordinary Brick-Clay, and with the Ash of a highly carbonised Bituminous Shale, occurring in close proximity to the Fire-clay.

Specific Gravity	Richardson.	A. W. Wills.											C. Tooley.		H. Taylor.	E. Riley.	J. Brown.		A. W. Wills.		Muspratt.
		1	2	3	4	5	6	7	8	9	10	11	12	13			14	15	16	17	
			2.51	2.54	2.38	8.47	2.49	2.48							2.519						
Silica . . . .	70.50	73.82	68.82	48.54	11.96	67.34	61.33	60.27	71.41	68.44	69.91	65.10	67.12	66.16	65.50	67.12	66.16	46.84	60.30	49.44	
Alumina . . . .	25.46	16.88	17.88	26.74	16.31	21.01	26.22	23.89	21.17	27.01	17.44	22.22	21.18	22.64	27.75	21.18	22.64	27.31	29.85	34.20	
Protoxide of iron	2.04	2.96	3.63	5.42	42.60	2.03	1.06	1.74	.91								5.31	1.66			
Seesquioxide iron		trace	trace	1.84	trace					2.47	2.89		1.85		2.01	1.85			3.14	7.74	
Lime . . . .		trace	trace	1.30	trace		.41	.72	.04	.73	3.08	0.14	0.32	1.42	0.67	0.32	1.42	0.20	2.19	1.48	
Magnesia	1.05	trace	trace	1.30	trace		.19	.66	trace	.19	4.47	0.18	0.84	trace	2.19	0.84	trace	0.92	1.63	5.14	
Alkalis . . . .		.90	1.19	.97	.07	1.38	.68	.95	.82	1.33	2.21	{	2.02		0.44	2.02		1.84	2.12		
Vanadium . . . .									trace									0.31			
Bisulphide iron					2.52																
Carbonic acid . . . .				.40	26.91													trace	0.69		
Sulphuric acid . . . .		trace	trace	trace			trace		trace												
Phosphoric acid . . . .										trace											
Chlorine . . . .		trace	trace	trace			trace		trace										0.31	0.06	
Organic matter							trace		trace										10.21		
Water, combined		{	6.45	8.48	15.79	.63	8.24	10.11	{	3.49					trace						
Do. hygroscopic								11.21		2.67					10.53			10.31		1.94	
																1.39					

1. Stourbridge Fire-clay.  
 2. Best Glass House Pot-clay, Tintam Abbey, Stourbridge.  
 3. Best Second Clay, Tintam Abbey, Stourbridge.  
 4. Weak, shaly clay, rejected as useless, Tintam Abbey, Stourbridge.  
 5. "Canoe," taken out of bed of clay, Tintam Abbey, Stourbridge.  
 6. Homer's best glass-house Pot-clay, Stourbridge.  
 7. Best clay from Ambleside.  
 8. Best clay from Delph Works, Stourbridge.  
 9. Best clay from Tamworth.  
 10. Potsherd, made from Stourbridge clay.  
 11. Fragment of a faulty pot, useless.  
 12. Best clay, used by Messrs. Chance (Percy's Metallurgy).  
 13. Clay from Newcastle on Tyne, used for bricks (Percy's Metallurgy).  
 14. Clay from Dowlais (Percy's Metallurgy).  
 15. Clay from Glasgow, well adapted for aggers, glass-house pots, crucibles, and bricks (Percy's Metallurgy).  
 16. Inferior clay, approaching to shale.  
 17. Residue from distillation of bituminous shale.  
 18. Brick-clay.

W. W.

**FIRE-DAMP.** The explosive mixture of marsh-gas and air, which accumulates in coal-mines. (See COAL.)

**FIRE-OPAL.** See OPAL.

**FIRE-STONE.** A stone which will bear the heat of a furnace without injury. The term is generally applied to the sandstone occurring at the top of the upper greensand in the south of England, which is frequently used for lining kilns and furnaces. (See *Ure's Dictionary of Manufactures*, &c. ii. 224.)

**FIRE-WORKS.** See PYROTECHNY.

**FIRE-WOOD.** See WOOD.

**FISCHERITE.** Native phosphate of aluminium from Nischne Tagilsk. (See PHOSPHATES.)

**FISH-OIL.** See OILS.

**FIXED AIR.** Carbonic acid gas.

**FIXITY.** The converse of volatility.

**FLAKE-WHITE.** A term applied indiscriminately to pure white lead, and to basic nitrate of bismuth.

**FLAME.** The nature of flame, and many of the conditions on which its heating and illuminating power depend, have already been considered in the article COMBUSTION (i. 1094-1102). We have here, however, to give an account of the results obtained by Frankland respecting the manner in which the heat and light of flames and of burning bodies in general are affected by the density of the surrounding air. (*Phil. Trans.* 1862, p. 629; *abstr. Proc. Roy. Soc.* xi. 137, 366.)

*Rate of Combustion.*—From comparative experiments made on the combustion of stearin candles on the summit of Mont Blanc and in the valley of Chamounix, and from further experiments on the burning of candles and coal-gas in artificially rarefied atmospheres, it is found that the rate of burning of candles and other bodies, the flames of which consist of matter volatilised, and subsequently burned in contact with the air, is not sensibly affected by the pressure of the medium which supports the combustion. But in self-supporting combustibles, like the time-fuses of shells, the rate of combustion depends essentially on the pressure of the medium in which they are deflagrated. This fact was first pointed out by Quarter-master Mitchell, an artillery officer stationed in India, who found that the fuses of shells burnt longer at elevated stations than when ignited near the sea-level. From his observations, and from experiments performed by Dr. Frankland on the combustion of time-fuses in artificially rarefied air, it is found, that in the combustion of shell-fuses, *the increments of time are proportional to the decrements of pressure*, each diminution of one inch of barometric pressure causing a retardation of one second in a thirty-second fuse; or each diminution of atmospheric pressure to the amount of one mercurial inch increasing the time of burning by one-thirtieth.

This remarkable difference in the influence of atmospheric pressure on the rate of combustion of candles, &c., on the one hand, and of self-supporting combustibles on the other, arises from the different conditions of combustion in the two cases. In the combustion of a candle there is, at all pressures, a sufficient supply of combustible matter kept up at the base of the exposed portion of the wick: for the capillarity of the wick is not affected by pressure, and the temperature of the flame remains nearly constant, the greater mobility of the gases in the rarefied atmosphere compensating for the smaller number of particles of oxygen within a given space: hence the rate of combustion is, within certain limits, independent of the pressure. In the fuse, on the contrary, the composition contains within itself the oxygen necessary for its combustion, and a certain degree of heat only is necessary to bring about chemical combination. If this heat were applied simultaneously to every part of the fuse-composition, the whole would burn almost instantaneously. Under ordinary circumstances, however, the fuse burns only at a disc perpendicular to its axis; and the time occupied in its deflagration depends on the rapidity with which each successive layer of the composition is heated to the temperature at which combustion takes place. This heat necessary to deflagration is derived from the products of the combustion of the layer immediately preceding, and the amount of heat thus communicated to the still unburnt layer, depends in a great measure, on the number of particles of these heated products which come into contact with that layer. Now, as a large proportion of those products are gaseous, it follows, that if the pressure of the surrounding medium be diminished, the number of ignited gaseous particles in contact at any one moment with the still unignited disc of composition will also be diminished. Hence the slower rate of deflagration in rarefied air.



*Influence of pressure on the Luminosity of Flames.*—On the summit of Mont Blanc, candles burned with a very feeble light, and subsequent experiments with ordinary coal-gas, and with naphthalised gas (which has twice as much illuminating power as common coal-gas), in artificially rarefied atmospheres, have shown that the brightness of ordinary flames increases and diminishes with the pressure of the supporting medium, and that, when the air is rarefied from the ordinary atmospheric pressure down to a pressure of 14 inches of mercury, the light of the flame decreases in exact proportion to the density of the air; below this limit, the luminosity diminishes at a somewhat lower rate. Between the limits of pressure above mentioned, the amount of diminution is expressed by the following law: *Of 100 units of light, emitted by a gas-flame burning in air at a pressure of 30 inches of mercury, 5.1 units are extinguished by each reduction of one mercurial inch of atmospheric pressure.*

Under increased pressure, the brightness of a flame fed with amyl alcohol, was found to increase in direct proportion to the pressure, up to a limit of 2 atmospheres; beyond which, the increase of light was much more rapid, and attended with a great deal of smoking.

The cause of these variations of luminosity is as follows. The light of ordinary flames is derived almost wholly from the separation of carbon particles within the flame, and is increased by the augmentation of the amount of carbon thus precipitated, and by an increased temperature in the flame\*, whilst it is diminished by the separation of less carbon (and, therefore, *ceteris paribus*, by more complete combustion) and by a reduction of temperature. Now Davy found, and his conclusion has been confirmed by Frankland, that, within certain limits, rarefaction and compression do not exert any considerable influence on the heat of flame: in fact, though the temperature produced within the flame is lowered by rarefaction, the escape of heat from its exterior is hindered by the same process, the result being that the actual temperature undergoes but little alteration. Hence the loss of light in rarefied air does not proceed from reduction of temperature. Neither is it due to imperfect combustion: for the gases evolved from a candle-flame, burning under a pressure of only eight mercurial inches, are found to have the same composition as those from a flame burning under the ordinary pressure. On the other hand, the separation of carbon particles is augmented by increased pressure. Candles evolve much smoke when burnt under a pressure of two atmospheres; and even a small alcohol flame, which burns with a pure blue light at ordinary pressures, becomes highly luminous in air four times compressed. Flames which smoke at ordinary pressures, become smokeless in rarefied air, and undergo more complete combustion. Whilst, therefore, the light of flames is due to the separation of carbon particles, the latter owe their momentary existence to the absence of sufficient oxygen for their combustion; consequently, any influence, which causes the more rapid interpenetration of the flame-gases and the external air, must reduce the amount of precipitated carbon, and consequently the luminosity of the flame. Rarefaction exercises precisely such an influence, by increasing the mobility of the gaseous particles, and thus causing the access of a larger amount of oxygen to the region of the flame where precipitated carbon produces luminosity.

The luminosity of a flame is not, however, entirely due to the ignition of minute carbon particles floating within it, a small portion of the light being derived from the incandescence of the gaseous matters. This latter source of illumination does not ordinarily furnish more than about 1 per cent. of the total amount of light, but at very low pressures, at which but little carbon is separated, it becomes much more prominent. Now this light emitted by incandescent gaseous particles is not affected by pressure, and hence arises the deviation from the law of diminution of light in proportion to pressure, which is observed when the pressure is reduced to a very small amount. (Frankland.)

**FLAVIN.** A yellow dye stuff imported from America, in the form of a dark brown powder, and used as a substitute for quercitron bark (*Napier's Manual of the Art of Dyeing*, Glasgow, 1853.) According to König (J. pr. Chem. lxxi. 98), it is identical with quercitrin, and splits up, under the influence of acids, into sugar and quercetin; but according to Bolley (Dingl. pol. J. cxlv. 134), it is not of constant composition, sometimes containing, not quercitrin, but quercetin, which possesses much greater colouring power.

**FLAVINDIN.** (Gerh. iii. 563.) A substance apparently isomeric with indin and indigo-blue, produced, together with hydrindin (*q. v.*), by the action of potash on indin or on disulphisathide. It remains in the alkaline mother-liquor from which the hydrindin has separated; and on adding an acid to this liquid, a light, flocculent, yellowish precipitate is obtained, which is a mixture of hydrindin, sulphur, sometimes a small quantity of indin, and flavindin. The flavindin may be obtained in larger quantity by

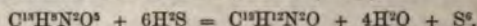
\* See the article COAL-GAS in *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 736.

continuing the ebullition with potash for a longer time; it is purified by solution in water containing a few drops of ammonia, and precipitation with hydrochloric acid.

Flavindin is of a pale yellow colour; it dissolves sparingly in boiling alcohol, and separates therefrom in microscopic stellate needles. When heated, it appears to be almost wholly transformed into a white substance, which sublimes in needles resembling benzoic acid.

Flavindin gives by analysis 72.5 per cent. carbon, and 3.82 hydrogen, whence it appears to have the same composition as indigo-blue. Its ammoniacal solution yields with nitrate of silver a yellow precipitate, which leaves on calcination 42 per cent. silver ( $C^8H^8AgNO^2?$ ).

**FLAVINE.**  $C^{12}H^{12}N^2O$ . (Laurent and Chancel, *Compt. Chim.* 1849, p. 115.) An organic base, isomeric with diphenyl-carbamide (i. 756), produced by the action of sulphhydrate of ammonium on dinitrobenzophenone (i. 662),



It forms fine, pale yellow, or colourless needles, nearly insoluble in water, but soluble in alcohol and ether. Gives off phenylamine when fused with potash.

*Hydrochlorate of Flavine* crystallises in elongated laminae, very soluble in water, somewhat less soluble in alcohol; it is decomposed by distillation, yielding a small quantity of white, pulverulent sublimate, and leaving a bulky residue of charcoal. The *chloroplatinate*,  $C^{12}H^{12}N^2O.HCl.PtCl^2$ , is a yellow, pulverulent precipitate, obtained from dilute solutions.

Flavine was regarded by Laurent and Chancel as identical with diphenylcarbamide,  $N^2(CO)''(C^6H^5)^2H^2$ ; but, according to Hofmann (*Proc. Roy. Soc.* x. 602), it does not exhibit the properties of a carbamide or urea.

**FLAX.** *Linum usitatissimum*. This plant is extensively cultivated in Ireland, Belgium, France, and Russia, both for its fibre, which is the raw material of linen, and for its seed, which yields by pressure a fixed oil, called linseed oil, and a residual mass, called linseed-cake, or oil-cake, extensively used as food for cattle. The flax-plant takes up from the soil a large amount of mineral matter, especially of the most valuable constituents, potash and phosphoric acid, and was therefore formerly regarded as one of the most exhausting crops. But neither the pure fibre nor the oil contains any of these mineral constituents. The inorganic matter of the seed remains in the cake, which, being used to feed cattle, may be returned to the soil as manure. On the Continent, inferior qualities of cake are ground to a coarse powder, and either applied to the soil as a top-dressing, or steeped in a liquid manure, and the mass spread out on the land in that state. (See LINSEED.)

The stem of the flax plant consists of an inner part or core, sometimes hollow, but more frequently solid, composed of ligneous matter, surrounded with a bark of fibres, the true linen fibres, which are united to each other by a gum, the whole being sheathed in a fine epidermis. To separate the linen-fibre from the gum and woody matter, the stems, when pulled and separated from the seed-capsules, are steeped in a pond or running stream, for a period varying from 7 to 21 days; they then undergo a kind of fermentation or putrefaction, attended with the evolution of sulphuretted hydrogen and other fetid gases, which decomposes the gum and loosens the fibres from one another and from the woody core; this process is called retting. The stems are then washed, and the fibre is mechanically separated from the woody core by an operation called scutching, which consists in bruising the stems thoroughly, so that, while the fibre, from its tenacity, remains intact, the brittle woody part is flattened and broken in such a manner as to admit of its being easily beaten off by the action of the scutch-blade or scutch-mill. The greater part of the mineral matter is removed in the steeping and wash-water, in which state of solution it is easily returned to the soil. Another portion remains attached to the woody matter, which is generally used as fuel, the mineral substances of course remaining in the ash, which may likewise be used as manure. By thus returning to the soil the mineral matters removed by the growing plant, flax may be rendered one of the least instead of one of the most exhaustive of agricultural plants.

The following analyses of the ash of the stem and seed of flax will show that it contains large quantities of alkali and phosphoric acid.

1-7. Belgian and Irish flax (Kane, *Phil. Mag.* [3] xxiv. 98; xxxi. 36, 105; *J. pr. Chem.* xxxii. 354; xli. 434; *Jahresber. d. Chem.* 1847-8, p. 1085).—8-11. Russian (Mayer and Brazier, *Chem. Soc. Qu. J.* ii. 78; *Jahresber.* 1849, p. 686).—12-18. English (Way and Ogston, *Roy. Agr. Soc. J.* ix. [2] 517; *Jahresber.* 1850, p. 669).—19-20. (Reich, *Jahresber.* 1850, p. 670).—21, 22, 24, 25. (Way and Ogston, *loc. cit.*)—23. Rammelsberg (*Jahresber.* 1847-8, p. 1075.)



TABLE I.—Composition of the Ash of the Stem and Seed of Flax.

	Potash, K <sub>2</sub> O	Soda, Na <sub>2</sub> O	Lime, CaO	Magne- sia, MgO	Alumi- na, Al <sub>2</sub> O <sub>3</sub>	Ferric oxide, Fe <sub>2</sub> O <sub>3</sub>	Mangan- ic oxide, Mn <sub>2</sub> O <sub>3</sub>	Sul- phuric oxide, SO <sub>3</sub>	Chloro- fine, SiO <sub>2</sub>	Carbon- ate oxide, CO <sub>2</sub>	Phos- phoric oxide, P <sub>2</sub> O <sub>5</sub>	Chloro- sium, KCl	Chloro- sodium, NaCl	Total		Ash per cent.		Nitrogen per cent.
														In substance undried, 100° C.	In substance dried at 100° C.	In substance undried, 100° C.	In substance dried at 100° C.	
Stem :																		
1. Wild flax of inferior quality . . . . .	7.70	19.19	15.38	3.44	0.44	4.50	trace	6.28	..	3.05	20.60	11.21	..	8.21	100.00	..	4.237	0.982
2. Cultivated, best quality, Belgium . . . . .	22.50	..	16.48	3.33	0.41	1.52	trace	6.17	..	3.41	25.23	11.80	..	8.70	99.95	..	5.434	0.756
3. Cultivated, best quality of the year, Belgium . . . . .	22.30	14.11	18.52	3.33	0.72	1.10	trace	6.83	..	2.68	16.38	8.81	..	4.58	99.99	..	3.670	0.876
4. Nearly wild . . . . .	25.79	0.43	19.10	3.65	..	2.28	..	12.09	..	3.03	9.89	10.98	..	12.75	99.99	..	4.940	0.901
5. Cultivated, Holland . . . . .	18.41	10.31	18.37	3.02	1.44	2.36	..	9.68	..	8.33	13.75	11.06	..	9.63	99.98	..	8.151	1.00
6. " near Dublin . . . . .	9.78	9.82	12.33	7.79	5.08	..	..	2.65	2.41	21.35	15.95	10.84	..	6.90	100.00	..	5.00	0.56
7. " County of Armagh . . . . .	6.33	6.35	22.70	4.06	..	13.52	1.09	8.93	..	24.98	4.11	7.00	1.31	..	99.97	..	5.572	0.627
8. "																		

\* ? Dried or undried.



In Kane's analysis, the amount of sulphuric acid varies inversely as that of the carbonic acid (*i.e.* of the organic acids); and notwithstanding the great variations in the relative quantities of the several bases (the ferric oxide in the variety from Armagh amounting to 13·52 per cent.), the capacity of the bases in the ash for organic acids is nearly the same in all, being represented by an amount of 13·28 per cent. oxygen in the Belgian and Dutch, and 13·53 per cent. in the Irish flax.

The results of Mayer and Brazier's analyses agree nearly with those of Kane, so far as regards the lime and phosphoric acid; but in all other respects they differ considerably. In most of Kane's analyses, the potash and soda are nearly equal; whereas in those of Mayer and Brazier, the potash greatly exceeds the soda. Kane also found alumina in most of his samples, whereas Mayer and Brazier, and indeed all other chemists who have analysed flax-ash, found none.

Analyses 12, 13 (Way and Ogston) show that the coarse-fibred varieties remove from the soil a larger quantity of potash and of mineral constituents in general than the fine-fibred kinds. In all cases, however, comparatively little of the more valuable mineral constituents remain with the scutched fibre, the greater part being dissolved out in the retting or steeping process, and another portion remaining with the woody matter separated by scutching.

The soils on which the samples of flax analysed by Kane were grown, were mostly sandy loams, very light and porous, rich in nitrogenous matter, and coloured the water in which they were boiled, small quantities of alkalis and salts then passing into solution. Their composition is given in the following table:

TABLE II.—Composition of Flax-soil.

	Soils dried at 100° C. from :					
	1 Heestert near Courtray.	2 Escamaffles, best flax- land of the Courtray district.	3 Hammezog, best flax-land of the Ant- werp dis- trict.	4 A district yielding only wild flax and poor crops.	5 A good flax dis- trict in Holland.	6 Crowle in Lincoln- shire, the so-called "warps."
Potash . . . .	0·160	0·123	0·068	0·151	0·583	0·534
Soda . . . . .	0·298	0·146	0·110	0·206	0·306	0·083
Ferric oxide . .	3·298	1·663	1·202	1·543	6·047	4·500
Manganic oxide	trace	trace	trace	trace	trace	strong tr.
Alumina . . . .	2·102	1·383	0·125	0·988	5·626	3·065
Lime . . . . .	0·357	0·227	0·481	0·366	3·043	5·538
Magnesia . . .	0·202	0·153	0·140	0·142	0·105	0·052
Sulphuric anhy- dride . . . . .	0·025	0·017	0·013	0·026	0·023	0·113
Phosphoric „	0·121	0·152	0·064	0·193	0·15	0·222
Chloride of So- dium . . . . .	0·017	0·030	0·067	0·009	0·023	0·067
Clay . . . . .	14·920	9·280	5·760	4·400	17·080	
Sand . . . . .	75·080	84·065	86·797	88·385	60·947	80·702
Organic matter; residual mois- ture . . . . .	3·123	2·361	4·209	3·672	5·841	5·328
Loss . . . . .	0·297	0·400	0·964	..	0·217	
	100·000	100·000	100·000	100·081	100·000	100·204

The samples 1-4 of flax in the table (p. 657) were grown on soil No. 4; sample 5 in the same table on soil No. 5.

The so-called "warps" is found on the river Humber, and forms the muddy bottom of the flax-lands of the west coast (of Ireland?).

Kane regards the fertility of the celebrated Belgian flax-soils, *i.e.* their great lightness, as well as their amount of alkalis, phosphoric acid, and magnesia, as the result of diligent cultivation with animal manure, such cultivation requiring only a light sandy soil, with enough loam to make it coherent.

TABLE III.—*Composition of Russian Flax-soils. Mayer and Brazier*  
(Chem. Soc. Qu. J. ii. 78).

	Liefland.	Kurland.	Lithuania.	Esthland.
Organic matter . . . . .	4.717	4.030	4.344	4.863
Soluble in dilute hydrochloric acid.	Sulphuric anhydride	0.154	0.088	0.121
	Phosphoric " . . .	0.140	0.054	0.080
	Ferric oxide . . .	1.807	2.377	3.190
	Manganic oxide . .	trace	trace	trace
	Alumina . . . . .	1.192	1.873	2.142
	Lime . . . . .	0.375	0.782	0.498
	Magnesia . . . . .	0.201	0.130	0.180
	Potash . . . . .	0.501	0.324	0.547
Insoluble in dilute hydrochloric acid.	Soda . . . . .	. . .	0.132	0.045
	Chloride of sodium	0.045	0.025	0.042
	Silica . . . . .	79.342	81.500	85.094
	Ferric oxide . . .	trace	trace	trace
	Alumina . . . . .	11.627	6.114	2.245
	Lime . . . . .	trace	1.873	0.878
	100.101	99.302	99.406	99.208

Mayer and Brazier also give the following as the result of treating these soils with water and hydrochloric acid, and determining directly the quantities of substance dissolved.

TABLE IV.—*Russian Flax-soils.*

	Liefland.	Kurland.	Lithuania.	Esthland.
Sol. in water { Mineral matter .	0.086	0.170	0.153	0.150
	{ Organic " . . .	0.229	0.312	0.442
Soluble in hydrochloric acid . .	0.315	0.482	0.595	0.608
	7.259	6.917	7.243	8.712
Insoluble residue . . . . .	92.425	92.601	92.162	90.681
	99.999	100.000	100.000	100.001

The proportions thus determined of matter soluble and insoluble in hydrochloric acid, do not quite agree with those found by the elementary analysis of the same soils given in the preceding table. All these soils are distinguished by their richness in alkali, especially potash, and in phosphoric acid.

TABLE V.—*Composition of Steep-waters.*

	100 pts. of evaporation-residue yielded :				
	1	2	3	4	5
Potash . . . . .	8.740	4.181	15.762	5.405	8.205
Soda . . . . .	28.620	11.607	30.232	28.298	19.277
Lime . . . . .	6.940	8.435	17.829	5.484	3.613
Magnesia . . . . .	0.856	1.369	1.530	1.192	7.601
Ferric oxide . . . .	0.514	6.633	2.584	6.200	1.183
Sulphuric anhydride	8.054	8.435	11.627	9.300	5.607
Phosphoric " . . .	. . .	. . .	. . .	0.079	. . .
Hydrochloric acid .	25.765	8.682	2.580	7.754	9.439
Carbonic anhydr. } organic matter, } and loss . . . . .	20.511	50.658	17.856	36.288	45.075
100,000 pts. water left on evaporation	100.000	100.000	100.000	100.000	100.000
	51.70	139.69	50.68	45.11	42.40

*Steep-water.*—Kane has analysed several waters (Table V.) in which flax is steeped. 1. Water of a large pool (forming a peat-bog) fed by the Scheldt, clear, with the exception of a small quantity of suspended matter.—2. Of a pool used for flax-steeping near Hammezog in Belgium, also fed by the Scheldt. The flax is left in it for six weeks. At the beginning of the process, the surface of the water becomes covered with a vegetable growth, which disappears as the retting proceeds: the workmen then shovel up the mud from the bottom, and make the flax sink with it; it was at this stage, that the sample of water, very muddy, was taken for analysis.—3. Another pool from a different part of the country, nearly clear.—4. From the river Lys, which rises in the north of France, and flows through the west of Belgium: it is regarded as the best steep-water in the world; and yet there is nothing in its chemical composition to account for its being so peculiarly favourable to the steeping of flax.—5. From Holland.

The following are two analyses of retting waters by C. Schmidt (Ann. Ch. Pharm. lxxxiii. 321); *a* from the Linnajerw-see surrounded by marshes, six miles south of Dorpat; it generally yields a beautifully white flax, but in windy weather somewhat coloured. *b* from the Kullajerw-see in the same neighbourhood; which being protected from the wind by surrounding woods, yields a uniform product. Both waters are clear and colourless, and leave, when evaporated, a brownish residue, which effervesces with acids, after being carbonised. 1 cubic metre of the water yielded the following quantities in grammes.

TABLE VI.—*Steep-waters.*

	<i>a.</i>	<i>b.</i>
Chlorine . . . . .	21·85	43·45
Sulphuric anhydride . . . . .	1·06	2·03
Phosphoric . . . . .	2·51	21·01
Potassium . . . . .	10·20	18·10
Sodium . . . . .	20·04	54·45
Lime . . . . .	4·13	10·67
Magnesia . . . . .	1·43	5·93
Ferric oxide . . . . .	1·36	6·12
Oxygen of the alkalis . . . . .	4·14	12·87
Inorganic matter . . . . .	66·72	174·68
Organic matter and ammonia . . . . .	68·10	99·62
Anhydrous substance . . . . .	134·82	274·30

*Hot-water steeping.*—The ordinary steeping process takes from one to six weeks, according to the temperature and state of the weather. In 1847, however, a new system of retting was introduced into Ireland, by Mr. Schenck of New York. This consists in immersing the flax-stems in a large tank containing water kept at the temperature of about 90° F., by means of a coil of pipe through which steam is passed. The higher temperature greatly accelerates the process, which is completed in about 40 or 90 hours, according as the water used is soft or hard. The gas evolved during the process is usually stated to contain sulphuretted hydrogen; but, according to Hodges, it consists in 100 vol. of 22·29 carbonic anhydride, 44·30 hydrogen, and 33·41 oxygen. Three samples, *A*, *B*, *C*, of scutched flax, which had been retted by this process, were found by Hodges (Chem. Gaz. 1854, p. 37; Brit. Assoc. Rep. 1857, p. 126; Jahresber. d. Chem. 1854, p. 800; 1858, p. 667) to have the composition given in the following table. All three samples were dried at 100° C.; *A* losing 9·10, *B* 8·61, and *C* 12·0 per cent. water:

	<i>A.</i>	<i>B.</i>	<i>C.</i>
Wax; volatile oil and acid; resin . . . . .	2·200	2·620	1·360
Sugar and substances soluble in alcohol . . . . .	1·541	0·624	5·630
Inorganic substances soluble in alcohol . . . . .	0·281	0·116	2·830
Gum and pectin . . . . .	0·698	0·280	0·360
Salts insoluble in alcohol . . . . .	0·076	0·044	0·080
Azotised substances soluble in water, casein, &c. . . . .	3·560	1·386	6·834
Azotised substances insoluble in water . . . . .	2·940	4·310	4·269
Inorganic substances united with the fibre . . . . .	0·238	1·490	2·500
Woody fibre . . . . .	87·974	89·136	82·137



A sample of Courtray flax, retted by the ordinary method and scutched, gave, when dried at 100° C. (with loss of 8·40 per cent. water), 2·30 per cent. wax and oil, 6·60 azotised substances, casein, &c. ; 7·69 gum, sugar, and colouring matter, 1·05 inorganic matter (ash), and 82·56 woody fibre.

The sample A of flax retted by Schenck's process, yielded (after drying at 100° C.) 1·40 per cent., B 1·64 per cent. ash, having the following composition:

K <sub>2</sub> O	Na <sub>2</sub> O	NaCl	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	CO <sub>2</sub>	SiO <sub>2</sub>
7·94	2·19	2·75	29·24	4·64	3·72	5·23	6·00	28·17	10·45 = 100·44
1·85	7·63	1·77	27·08	0·70	7·40	10·40	3·12	19·10	21·31 = 100·52

Several methods have been proposed for disintegrating flax fibre by mechanical means, without previous fermentation, and cleansing it by the use of acids and alkalis; but they have not been adopted in practice to any great extent. For a description of these methods, and for full details relating to the mechanical operations to which the fibre is subjected to convert it into linen, the reader is referred to the excellent article on FLAX in *Ure's Dictionary of Arts, Manufactures, and Mines*, ii. 225.

**FLESH.** The flesh of animals is, anatomically considered, a complex tissue made up of several morphological elements, viz. true muscular fibre, connective tissue, nerves, blood-vessels, and lymphatics. Muscular fibre is of two kinds, striped or striated, and non-striated or plain; the former constituting the basis of the voluntary muscles; the latter occurring in the muscular coat of the stomach and intestines, and in several other viscera. The primitive bundles of striped fibre are enclosed in a thin horny tissue, called the sarcolemma; a number of these bundles are united by connective tissue into larger bundles, and these again into entire muscles, the connective tissue being more or less filled up with fat-cells. The plain or non-striated fibres have either no sarcolemma, or a very indistinct one, not generally recognised, and are merely joined together by connective tissue. The entire mass of a muscle, whether striped or plain, is moistened with an acid liquid called the flesh-juice or muscular juice; which, however, is much more abundant in the striped than in the plain muscles.

The chemical differences between striped and plain muscular fibre will be considered in the article MUSCULAR TISSUE. At present we shall treat of the flesh as a whole, as it is used for food.

TABLE I.—Composition of Muscular Flesh, according to Von Bibra. (*Traité de Chimie générale, par Pelouze et Frémy*, vi. 253.)

Name of Animal.	Muscular fibre, vessels, nerves, &c.	Albumin.	Hæmatoin.	Aqueous extract with salt.	Alcoholic extract with salt.	Phosphate of Calcium and Animal matter.	Albumin soluble in the connective tissue.	Fat.	Water.	Loss.
Man: pectoral muscles . . .	16·83	1·75		2·80		1·52	4·24	72·46		
Woman: „ . . .	15·54	1·93		3·71		2·07	2·30	74·45		
Ox: muscles . . .	17·05	2·20		1·8	1·3	traces			77·20	
Wild duck: pectoral muscles . . .	17·68	2·68		4·12		1·23	2·53	71·76		
Carp: heart . . .	2·0	5·26*		1·7	1·0				90·10	
Stag: „ . . .	18·0	2·30*			2·4	0·4			76·90	
Cat: muscles . . .	16·33	2·0		2·93		1·79	1·80		78·15	
Kid: „ . . .	18·00	2·3		2·80					76·90	
Pig: heart . . .	16·80	2·40*		0·8	1·7				78·39	
Cyprinus muscus: muscles . . .	9·42	1·38		4·36		2·13	0·54	82·17		
Viper: muscles . . .	13·36	1·35		4·93		2·80	1·32	76·19		
Falcon: heart . . .	17·59	1·08		7·33		2·70		71·30		
Frog: pectoral muscles . . .	11·77	1·86		3·46		2·48	0·10	80·33		
Swallow: muscles . . .	16·27	2·69		6·97		6·88	2·25	64·96		
Marten: muscles . . .	15·74	1·99		3·13		2·11	2·03	75·00		
Sparrow „ . . .	15·98	1·69		7·49		2·50	2·02	70·32		
Pigeon: heart . . .	17·0	4·5*		1·5	1·0			76·00		
Chicken „ . . .	16·50	3·0*		1·2	1·4	0·6		77·30		
Chicken: muscles . . .	16·50	3·0		1·2	1·4	0·6		77·30		
Trout: heart . . .	11·10	4·4		0·2	0·6	2·2		81·50		
Fox: muscles . . .	15·53	2·89		4·30		1·98	2·47			

\* The asterisks indicate that the albumin was not coagulated, and contained a portion of blood-clot.

Marechal (Compt. rend. xxxiv. 591) has determined the proportion of water, dry muscular substance, and fat in 100 pts. of the muscular flesh—free from connective tissue, bone, &c.—of the following animals, commonly used as food :

	Pig.	Ox.	Sheep.	Fowl.	Calf.
Water . . . . .	69.7	72.5	73.6	73.7	74.4
Muscular flesh free from fat	24.3	25.0	23.4	24.9	22.7
Fat . . . . .	6.0	2.5	3.0	1.4	2.9

It appears, from these results, that the flesh of the ox contains the largest proportion of nutritive (flesh-forming) matter, and in decreasing series, that of the fowl, pig, sheep, and calf. This must, however, be understood as applying to the real muscular substance, not to the entire flesh as sold in the market.

Girardin (Compt. rend. xli. 746) has determined the composition of American salt beef and bacon (imported into France in 1855) as compared with French beef and bacon.

TABLE II.—Composition of Salt Beef and Bacon.

	Salt Beef.				Bacon.			
	French.		American.		French.		American.	
	Fresh.	Dried at 100° C.	As taken from the cask.	Dried at 100° C.	Fresh.	Dried at 100° C.	As taken from the cask.	Dried at 100° C.
Water . . . . .	75.90	. .	49.11	. .	69.55	. .	44.06	. .
Fibrin and connective tissue	15.70	65.14	24.82	48.78	9.53	31.30	21.28	38.03
Fat . . . . .	1.01	4.19	0.18	0.35	11.77	38.65	7.01	12.53
Albumin . . . . .	2.25	9.34	0.70	1.38	3.20	10.51	0.40	0.71
Extractive matter . . . . .	2.06	8.55	3.28	6.44	3.45	11.33	3.91	6.99
Soluble salts . . . . .	2.95	12.24	21.07	41.39	1.64	5.39	22.82	40.78
Loss . . . . .	0.13	0.54	0.84	1.66	0.86	2.82	0.52	0.96
Sum . . . . .	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Nitrogen per cent. . . . .	3.00	12.58	4.62	9.10	3.73	12.26	3.20	5.73
Phosphoric acid (P <sub>2</sub> O <sub>5</sub> ) p. c. . . . .	0.22	0.93	0.62	1.22	0.55	1.81	0.33	0.59
Chloride of sodium per cent. . . . .	0.49	2.03	11.52	22.6	0.50	1.63	11.61	20.74

In the dark brown brine in which the beef from America had been salted, Girardin found 62.23 per cent. water, 1.23 albumin, 3.40 other organic substances (total amount of nitrogen 0.267 per cent.), 0.4 phosphoric acid, 29.01 chloride of sodium, 3.65 other salts.

TABLE III.—Composition of Lean and Fat of Pork, salted and unsalted (Lassaigne, J. Chim. méd. [3] ix. 155).

100 pts.	contain			
Flesh of ham (lean) . . . . .	71	water, 28.5	organic substance, 0.5	NaCl, KCl <i>a</i>
Breast marbled with fat . . . . .	29	"	70.6	" 0.4 " <i>b</i>
Back . . . . .	60	"	39.6	" 0.4 " "
Unsalted fat . . . . .	10	"	89.7	" 0.3 " "
Salted fat . . . . .	8.8	"	83.3	" 7.9 "NaCl"
Salted lean . . . . .	56.8	"	28.8	" 14.4 " "

*a* and *b*, together with alkaline carbonates.

For the results of Lawes and Gilbert's researches "On the Composition of some of the Animals fed and slaughtered as Human Food" (Proc. Roy. Soc. ix. 348), see NUTRITION.

TABLE IV.—*Composition of the Flesh of Fish*  
(Payen, Compt. rend. xxxix. 318).

	Water.	Dry substance.	Fat.	Inorganic substances.	Nitrogen.
Ray . . . . .	75.489	24.511	0.472	1.706	3.846
Conger-eel . . . .	79.909	20.091	5.021	1.106	2.172
Salt cod . . . . .	47.029	52.971	0.383	21.320*	5.023
Salt herring . . . .	48.998	51.002	12.718	16.433†	3.112
Fresh herring † . .	70.000	30.000	10.300	1.900	2.450
Whiting . . . . .	82.950	17.050	0.383	1.083	2.416
Mackerel . . . . .	68.275	31.725	6.758	1.846	3.747
Sole . . . . .	86.144	13.856	0.248	1.229	1.911
Dab . . . . .	79.412	20.588	2.068	1.936	2.898
Salmon . . . . .	75.704	24.296	4.849	1.279	2.095
Pike . . . . .	77.530	22.470	0.602	1.293	3.258
Carp . . . . .	79.968	23.032	1.092	1.335	3.498
Barbel . . . . .	89.349	10.651	0.212	0.900	1.571
Bleak . . . . .	72.889	27.111	8.134	3.253	2.689
Eel . . . . .	62.076	37.924	23.861	0.773	2.000
Gudgeon . . . . .	76.889	23.111	2.676	3.443	2.779

100 parts of the dried flesh, free from fat, of the following fish, were found by Payen to contain :

	Carbon.	Hydrogen.	Nitrogen.	Oxygen.	Ash.
Eel . . . . .	52.999	7.474	14.644	19.296	5.687
Mackerel . . . . .	51.515	6.902	15.836	19.603	6.139
Sole . . . . .	48.795	6.581	15.460	20.032	9.132
Barbel . . . . .	45.927	6.800	15.535	22.783	8.955

The following analyses by Schmitz and Mulder (*Traité de Pelouse et Frémy*, vi. 254) exhibit the elementary composition of the muscular flesh of certain fishes, free from fat and inorganic matter.

TABLE V.—*Muscular Flesh of Fishes.*

	Schmitz.						Mulder.		
	<i>Asineus fluviatilis.</i>		<i>Melolontha vulgaris.</i>		<i>Anodonta cygnea.</i>		<i>Solia vul-garis.</i>	<i>Rhom-bus bar-batus.</i>	<i>Gadus Mer-langus.</i>
	Carbon . .	Hydrogen . .	Nitrogen . .	Oxygen . .	Sulphur . .				
Carbon . .	52.14	52.39	52.35	52.08	52.40	52.50	53.14	53.69	
Hydrogen . .	7.10	7.18	7.20	7.14	7.34	7.26	6.99	7.11	
Nitrogen . .	15.22	15.44	15.20	15.34	15.33	. .	15.49	15.40	12.50
Oxygen . .	25.54	24.99	25.25	25.44	24.93	. .	0.84		
Sulphur . .	. .	. .	. .	. .	. .	. .			
	100.00	100.00	100.00	100.00	100.00				

*Inorganic constituents of Flesh.*—The quantity of ash left by muscular flesh appears to vary between 2 and 8 per cent. The ash is composed chiefly of alkaline and calcic phosphates, with smaller quantities of chloride, sulphate, and carbonate of sodium.

The following tables exhibit the composition of the ash of various kinds of flesh.

\* Including 19.554 chloride of sodium.

† Including 14.623 chloride of sodium.

‡ Calculated approximately from the composition of the salted herrings.



TABLE VI.—Ash of Muscular Flesh (Von Bibra, *loc. cit.*).

Name of Animal.	Per-centage of ash in dried muscular fibre.	Composition of the ash.				
		Chlo-ride of sodium.	Sul-phate of sodium.	Alkaline phos-phates.	Earthy and fer-ric phos-phates.	Carbo-nate of sodium.
Man, aged 30 years: muscles . . .	. .	10.30	1.72	72.95	15.03	
Man, aged 59 years: pectoral muscles . .	. .	traces	11.40	69.03	19.57	
" " heart . . .	. .	3.48	4.26	63.68	28.58	
Woman, aged 36: pectoral muscles . .	4.80	13.44	1.86	63.58	21.12	
" " heart . . .	3.61	5.33	traces	84.14	10.53	
Infant, a week old: muscles . . .	. .	6.33	2.04	81.44	10.19	
Ox: muscles . . .	7.71	6.50	0.30	76.80	16.40	
Budger, female: muscles . . .	6.16	4.04	. .	85.96	10.00	
Wild duck: muscles . . .	4.48	1.20	. .	84.00	14.89	
" " muscular membrane of stomach . . .	5.40	. .	traces	87.90	12.10	
Carp ( <i>Cyprinus Carpio</i> ) . . .	6.16	1.31	12.30	44.19	42.20	
Cat, male: muscles . . .	5.36	3.17	. .	74.13	20.70	2.00
" " muscular tissue of stomach . . .	4.54	12.02	5.00	71.78	10.60	
" " heart . . .	4.49	1.31	. .	88.85	9.84	traces
" female: muscles . . .	4.81	0.55	traces	74.05	25.40	
" " muscles of stomach . . .	2.92	1.00	. .	46.30	52.70	
" " mucous membrane of stomach . . .	2.26	1.70	. .	23.30	75.00	
Kid, female: muscles . . .	4.68	1.00	. .	72.00	20.60	
" " heart . . .	5.06	1.73	. .	70.07	28.20	
Raven: pectoral muscles . . .	7.46	5.34	1.23	85.33	8.10	
" " heart . . .	4.68	3.34	. .	70.06	17.60	traces
" " muscles of the thigh . . .	4.74	4.66	0.97	86.03	8.34	
Turkey: muscles . . .	4.30	16.63	22.20	33.25	1.46	10.46
Squirrel: " . . .	5.49	3.04	traces	85.54	11.42	
Falcon ( <i>Falco pyrrargos</i> ): muscles . .	4.73	1.15	. .	90.40	8.45	traces
" " muscular membrane of stomach . . .	2.82	traces	. .	57.90	42.10	traces
" " mucous membrane of stomach . . .	4.95	1.39	. .	81.21	17.40	trace
Falcon ( <i>Falco hucto</i> ): muscles . .	4.66	7.38	4.50	46.15	41.97	
" " muscular membrane of stomach . . .	4.95	1.39	. .	81.21	17.40	trace
" " mucous membrane of stomach . . .	8.97	2.07	4.32	51.11	20.50	trace
Frog ( <i>Rana esculenta</i> ) . . .	4.96	11.00	. .	64.00	25.00	trace
Owl: muscles . . .	4.40	trace	trace	76.40	23.60	trace
" " muscular membrane of stomach . . .	4.05	trace	4.40	49.00	46.60	trace
" " mucous " " . . .	7.36	trace	33.00	31.30	35.70	trace
Hare, male: muscles . . .	4.48	4.20	0.90	79.80	15.10	
Marten, male: muscles . . .	4.42	5.55	2.18	54.62	37.65	
Hawk (starved to death) . . .	5.87	5.94	. .	69.33	24.35	trace
Perch ( <i>Perca fluviatilis</i> ) . . .	7.08	1.27	. .	54.39	44.34	trace
Domestic fowl: pectoral muscles . .	5.51	1.39	trace	84.72	13.89	
" " muscular membrane of stomach . . .	6.34	18.45	4.33	63.52	13.70	trace
" " four years old . . .	3.14	1.30	. .	86.70	12.00	
" " thirteen years old . . .	4.31	trace	. .	87.10	12.90	
Fox, female: muscles . . .	3.85	1.02	2.50	74.08	24.40	
" " muscular membrane of stomach . . .	2.66	4.12	4.62	46.36	46.90	
" " mucous membrane of stomach . . .	5.24	8.96	. .	75.54	23.50	
Calf: muscles . . .	. .	trace	trace	89.80	10.20	

The following table contains analyses of the ash of various kinds of flesh used as food.—Ash of fresh beef: *a.* by Stölzel (Ann. Ch. Pharm. cxxvii. 266).—*b.* by

Staffel (Arch. Pharm. [2] lxiv. 148).—Of veal by the same.—Of fresh pork by Echevarria (Ann. Ch. Pharm. lxxxi. 373).—Of salt beef and ham, by Thiel (*ibid.* 370).—Of salt cod (stockfish), by Stölzel, *loc. cit.*

TABLE VII.—Ash of Meat, Salt and Fresh.

	Fresh.				Salt.		
	Beef.		Veal.	Pork.	Beef.	Ham.	Cod.*
	<i>a</i>	<i>b</i>					
Potash . . . . .	35.94	2.61	34.40	35.83	24.70	6.81	3.70
Soda . . . . .		34.91	2.35	4.31	16.82	34.06	4.26
Chloride of sodium . . . . .		7.49	10.59				16.11
Chloride of potassium . . . . .	10.22	4.01				0.10	
Lime . . . . .	1.73	5.09	1.99	7.15	0.73	0.41	40.22
Magnesia . . . . .	3.31	2.35	1.45	4.56	1.90	0.54	3.27
Ferric oxide . . . . .	0.98	0.96	0.27	0.33			0.54
Chlorine . . . . .				0.59	25.95	53.72	
Sulphuric anhydride . . . . .	3.37	1.77			0.62	0.12	1.64
Phosphoric " . . . . .	34.36	39.28	48.13	42.16	21.41	4.72	16.78
Ferric phosphate . . . . .					1.04	0.10	
Carbonic anhydride . . . . .	8.02						13.56
Silicic " . . . . .	2.07	1.52	0.81		0.20		
Charcoal . . . . .				0.51			
Sand . . . . .				2.74	5.50	0.23	
	100.00	99.99	99.99	98.18	98.87	100.81	99.08
Ash, per cent. in dry substance . . . . .		2.2	3.1				
Water in fresh substance . . . . .		72.63	77.64				

R. Weber (Pogg. Ann. lxxvi. 372; lxxxi. 92) analysed the ash of horse-flesh in two ways: *a*. By lixiviating the charred flesh with water, then with hydrochloric acid, and incinerating both the extracts and the solid residue. — *b*. By lixiviating the uncharred flesh with water and with hydrochloric acid, then carbonising and incinerating it; also incinerating the extracts. In both cases the flesh operated on was that of the fore-leg of a lean horse, freed from blood by injection with water. The composition of the total quantity of ash (solid residue and extracts) obtained in the two cases was as follows:

	NaCl	Na <sub>2</sub> O	K <sub>2</sub> O	Ca <sub>2</sub> O	Mg <sub>2</sub> O	Fe <sup>2</sup> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	
<i>a.</i>	1.47	4.86	39.95	1.80	3.88	1.00	46.74	0.30	= 100.00
<i>b.</i>	7.21	6.08	34.45	2.33	3.46	0.98	45.21	. .	= 99.72

The total quantity of ash obtained by the second method amounted to 0.85 per cent. of the fresh flesh, and 4.14 per cent. of the flesh dried at 100° C. 77.63 per cent. of the ash was contained in the aqueous extract, 18.45 in the hydrochloric acid extract, and 3.92 in the residue.

**FLESH-JUICE.** It has been stated in the preceding article that the muscular flesh of animals of the higher orders is moistened with an acid liquid, which is more abundant in the striped than in the plain muscles. This liquid has been examined chiefly by Liebig (Ann. Ch. Pharm. lxii. 257), Scherer (*ibid.* lxix. 343), and Strecker (Chem. Soc. Qu. J. x. 121). It is of reddish colour, reddens litmus paper strongly, and is partially coagulated by heat. It contains albumin, casein, creatine, creatinine, sarcosine, lactic acid, inosic acid, several volatile acids of the series C<sup>n</sup>H<sup>2n+1</sup>O<sub>2</sub>, among which, formic, acetic, and butyric, are the most conspicuous, a red pigment, similar to, but, according to Lehmann, not identical with, the colouring matter of the blood, and inorganic salts, chiefly alkaline chlorides and phosphates.

A small portion of the flesh-juice runs out on pressure, but the greater part remains in the tissue, and can only be extracted by treatment with water. The mode of obtaining it, and separating the creatine from it has been already explained (see CREATINE, ii. 95, *b*). The albumin separates on boiling; the casein is detected by acetic acid, or by the application of rennet, either of which produces turbidity.

The mother-liquor from which the creatine has crystallised, if further evaporated, mixed with small portions of alcohol till milky turbidity is produced, and then left to stand for some days, deposits yellow or white granular, laminar, or needle-shaped crystals, which are a mixture of creatine, phosphate of magnesium (if the phosphoric

\* The flesh was soaked in lime-water and washed.

acid has not been previously quite separated by baryta, ii. 95), and the potassium and barium-salts of inosic acid,  $C^5H^4N^2O^6$  (?).

On mixing the liquid from which the inosates have separated, with about five times its volume of alcohol, it separates into two layers, the lower of which is thick, syrupy, and brownish-yellow, and the upper more mobile and amounting to 20 times the volume of the lower. The heavier liquid cooled to  $-5^{\circ}C$ . deposits a large quantity of crystals of chloride of potassium. If separated from the lighter liquid and mixed with an equal volume of common ether, it becomes milky, and, on leaving it at rest, there gradually collects at the bottom of the vessel an amber-yellow syrupy liquid consisting almost wholly of lactate of potassium. The supernatant liquid also contains a little of this salt, but is chiefly a solution of creatinine.

If the liquid from which the inosates have separated be evaporated over the water-bath, and the residue treated with alcohol, all the lactates are dissolved; and if the alcoholic solution be separated from the insoluble syrup, and the alcohol evaporated, there remains a yellow syrup, which, after a week or ten days, solidifies to a soft crystalline mass, consisting of creatine, creatinine, and the potassium-salt of a nitrogenous acid, different from inosic acid; the mother-liquor contains lactate of potassium. As the lactic acid from flesh-juice exhibits certain peculiarities, it is sometimes called sarcocollactic acid. (See LACTIC ACID.)

When the hot mother-liquor of creatine (ii. 95, b) is diluted and mixed with acetate of copper, or better with nitrate of silver, a precipitate is formed, containing, together with other substances, a compound of sarcine with the oxide of copper or oxide of silver, which, when decomposed by sulphydric acid, yields sarcine,  $C^6H^9N^3O$ , in the form of a white, indistinctly crystalline powder. (Strecker.)

*Inorganic constituents of Flesh-juice.*—The juice, when evaporated to dryness and incinerated, yields an ash, difficult to burn white, and consisting of alkaline phosphates and chlorides. The soluble salts extracted from it by water contain the three modifications of phosphoric acid. (Liebig.)

The flesh-juice of all animals is very rich in potash; it contains chloride of potassium and only a small quantity of chloride of sodium; in the blood the proportion between these alkalis is reversed. It appears, from numerous determinations made by Liebig, that the quantities of potash present in the blood of certain animals, for 100 pts. of soda, are as follows:—

	Hen.	Ox.	Horse.	Fox.	Pike.
In the blood . . .	40.8	5.9	9.5		
In the flesh-juice . .	381.0	279.0	285.0	214	497

F. Keller (Ann. Ch. Pharm. lxx. 91) has examined the ash of the decoction of flesh [of what kind?], and that of the boiled flesh. Of the total quantity of ash obtained, 82.2 per cent. came from the decoction and 17.8 per cent. from the boiled residue.

	Ash of decoction.		Ash of residue.		Total amount of ash.	
	In water :		In water :		In decoction.	In residue.
	Soluble.	Insoluble.	Soluble.	Insoluble.		
$P^2O^5$ . . .	23.55	2.72	5.92	32.48	21.59	6.83
{ Cl . . .	8.25	0.38	. . .	. . .	7.09	
{ K . . .	8.98	0.42	. . .	. . .	7.72	
{ $SO^3$ . . .	3.21	0.38	. . .	. . .	2.95	
{ $K^2O$ . . .	3.78	0.45	. . .	. . .	3.47	
$K^2O$ . . .	34.18	4.69	6.76	20.13	31.95	4.78
{ $2Ca^2O$ . . .	. . .	3.06	0.29	9.05	2.51	1.66
$P^2O^5$ { $2Mg^2O$ . . .	. . .	5.76	0.57	16.26	4.73	2.99
{ $2Fe^2O^3$ . . .	. . .	0.57	0.05	7.97	0.46	1.42
	81.95	18.43	13.59	85.89	82.47	17.68
	100.38		99.48		100.15	

From these analyses, it appears that of the inorganic salts contained in meat nearly four-fifths are extracted by boiling with water. Part of the earthy and ferric phosphates passes into solution through the medium of the alkaline phosphates; but meat, even after long boiling, is still rich in alkaline phosphates, although the earthy phosphates predominate.



**Broth.**—When meat is boiled with water, sulphhydrate of ammonium is evolved, together with odoriferous compounds and an acid resembling acetic acid. The extract, called *broth*, contains fat, a portion of the odoriferous compounds just mentioned, gelatin, soluble salts, and the various proximate principles existing in the meat. The following is its composition, according to Chevreul.

Water			988.57
Fixed organic matters dried at 20° C. in vacuo			12.70
Soda	}		2.90
Potash			
Sulphuric and phosphoric acids, chlorine			
Phosphate of magnesium			0.23
Phosphate of calcium	}		0.10
Oxide of iron			
			1004.50

Boiled meat retains the fibrin, together with part of the albumin, and the earthy and ferric phosphates contained in the raw meat.

The quality of the broth and of the boiled meat depends greatly on the mode of boiling. To make good broth, the meat should be placed in cold water and gradually raised to the boiling heat. By this means, the soluble constituents of the meat are extracted before the albumin has time to coagulate in the tissue and oppose their extraction. In fact the coagulation of the albumin then takes place in the liquid only, not in the substance of the meat; and as the albumin becomes insoluble, it rises to the surface, carrying with it certain calcium-salts which would render the broth turbid, and forms a *scum* which prevents the volatilisation of the odoriferous matters. To obtain savoury and nutritious boiled meat, the meat should be at once plunged into boiling water, so that a thin layer of coagulated albumin may at once form on the surface and retain the soluble matters within the tissue.

The broth does not, however, contain the whole of the substances extracted from the meat by boiling, inasmuch as a portion of these substances undergoes decomposition and produces the aroma; hence, boiled meat and its broth taken together, are, for the same weight, somewhat less nutritious than roast meat.

**Liebig's Broth for invalids.**—Half a pound of finely chopped meat (beef or poultry), from a recently killed animal, is macerated for an hour with 1½ lb. cold distilled water to which 4 drops of pure hydrochloric acid and a drachm of common salt have been added; the liquid is then separated from the residue by straining, without pressure, through a hair-sieve, and the residue is still further exhausted by gradually pouring on it half a pound of distilled water. In this way, a pound of cold meat-extract is obtained, of reddish colour and agreeable taste. It must be taken cold, as, if heated, it becomes turbid, and deposits a thick coagulum of flesh-albumin and blood-red. The advantages of this mode of preparation are that it yields an extract containing certain ingredients which are wanting in ordinary broth prepared by boiling, those, namely, which serve for the formation of blood-albumin. Besides flesh-albumin, it contains a certain quantity of blood-red, and a much larger quantity of iron (which is necessary for the formation of blood-corpuscles), besides the hydrochloric acid, which assists the digestive process.

In warm weather this extract ferments, though without any bad odour. It should therefore be prepared with quite cold water in a cool place. (Liebig, *Ann. Ch. Pharm.* lxxvii. 350.)

**FLEXIBLE SANDSTONE.** A fissile variety of sandstone, thin slabs of which exhibit a certain degree of flexibility, apparently owing to the dissemination of small scales of mica through the mass. Sandstones of this character occur at Villa Rica, Brazil, and in the gold region of North Carolina.

**FLEXIBLE SILVER-ORE.** See STERNBERGITE.

**FLINT.** A variety of quartz, somewhat allied to chalcedony, but more opaque and of dull colour, usually grey, smoky brown, and brownish black, occasionally with zoned and striped delineations. It occurs in nodules embedded in chalk. Internal lustre barely glimmering, subvitreous. Fracture conchoidal. Fragments sharp-edged. Translucent. Harder than rock-crystal. Easily frangible. Sp. gr. 2.59. Infusible without addition, but whitens and becomes opaque. It consists mainly of silica (about 98 per cent.), with small quantities of lime, alumina, oxide of iron and water. The flint of the chalk-formation consists largely of the remains of infusoria, sponges, and other marine productions. The silica of flint, according to Fuchs, is partly soluble silica, easily taken up by a solution of potash. When two pieces of flint are rubbed together in the dark, they phosphoresce, and emit a peculiar smell.

**FLINTY SLATE.** See SLATE.

**FLOATSTONE.** A light spongy variety of quartz, the *quartz nectique* of Haüy, consisting of fibres or filamentary crystals aggregated into a spongy or porous mass, and so light as to float on water. Colour, white of various shades. It occurs in the chalk formation of Méné-Montant, near Paris, and in some of the Cornish mines.

**FLOS FERRI.** A coralloidal variety of arragonite occurring in beds of iron-ore.

**FLOUR.** The powder of the graminaceous seeds. (See *BREAD* and *WHEAT*; also *Ure's Dictionary of Arts, &c.*, ii. 277.)

**FLOWERS, COLOURS OF.** (Schübler, Schw. J. xvi. 285.—Decandolle, *ibid.* lv. 472.—Clamor-Marquart, *Die Farben der Blüthen*, Bonn, 1835. Frémy and Cloez, J. Pharm. [3] xxv. 249. Martens, Institut 1855, p. 168. Filhol, Compt. rend. xxxix. 194; l. 345, 1132; Jahresber. d. Chem. 1860, p. 535.)—The petals of flowers, while still enclosed in the bud, are mostly green, and acquire their characteristic colours only under the influence of light. Sometimes, however, they are white in the first instance, or the buds exhibit the same colours as the expanded flowers. The blue and red pigments of flowers are generally soluble in water, whereas many of the yellow pigments are of resinous nature and dissolve only in alcohol and ether. Schübler and Decandolle endeavoured to prove the existence of two essentially different series of flower colours, the xanthic, producing the yellow tints with their transitions into red, and the cyanic, producing the blue tints with their modifications; and that the colours of both series are formed from chlorophyll, the xanthic by oxidation, the cyanic by deoxidation; but these views are not borne out by observation.

The extractive blue, violet, and red pigments, which are likewise contained in brown and orange-coloured flowers, were designated by Clamor-Marquart, as anthocyan, the resinous yellow pigment as anthoxanthin. According to Frémy and Cloez, blue flowers contain a colouring matter, called cyanin (ii. 274), which is identical with Marquart's anthocyan, and occurs also, coloured by acids, in red flowers. Yellow flowers on the other hand contain two distinct colouring matters, xanthin and xanthein, the former insoluble, the latter soluble in water.

According to Martens, all plants secrete, in cells situated in the parenchyma below the epidermis, a pale yellow juice, which becomes continually darker in colour by the action of air and light, and sometimes gradually turns red. This extractive matter, likewise called xanthein by Martens, is generally associated in plants with a blue pigment, the anthocyan of Marquart and the cyanin of Frémy. Alkalis turn cyanin green, and deepen the yellow colour of xanthein.

According to Filhol, nearly all flowers contain a substance which forms colourless solutions with acids, and acquires a fine yellow colour when treated with alkalis: this substance was designated by Marquart as resin of flowers, and by Hope (J. pr. Chem. x. 269) as xanthogen (*q. v.*), which name is also retained by Filhol. He describes it as solid, of a light yellow colour, with faint greenish iridescence, soluble in water, alcohol, and ether, and very much like luteolin, with which it is associated in weld (*Reseda lutea*), but neither crystalline nor volatile. Xanthogen is not contained in mosses, in plants which grow in the dark, or in the flowers of *Pelargonium zonale*, *P. inquinans*, *Papaver Rhæas*, or the various species of *Salvia* and *Camellia*. All these flowers, when treated with alkalis assume a blue or violet colour, without any admixture of green, and the colouring matter contained in them is much more stable than that of most other flowers.

The xanthein (*q. v.*) of Frémy and Cloez exists also, according to Filhol, in many flowers either alone or associated with cyanin. The xanthin of the same chemists exhibits peculiar relations to chlorophyll. Its alcoholic solution is coloured green slowly by dilute, quickly by concentrated hydrochloric acid, and the liquid, if exposed for some time to the air, turns yellow and deposits a blackish substance which dissolves with blue colour in alcohol and ether. By agitation with a mixture of hydrochloric acid and ether, it is still more quickly resolved into a blue and a yellow colouring matter. Both xanthin and chlorophyll treated with hydrochloric acid containing a trace of nitric acid yield a nearly pure blue. Xanthin is less easily altered by sunshine than chlorophyll.

Certain yellow flowers, especially those of *Crocus luteus*, contain a peculiar colouring matter, which is amorphous, of golden-yellow colour, soluble in water and in alcohol, insoluble in ether, distinguished from xanthin by its solubility in water, and by not being perceptibly altered by hydrochloric acid.

The cyanin of blue and red flowers (ii. 274) is free from nitrogen and identical with the colouring matter called onolin or onocyanin, obtained by Glénard from red wine. The cyanin of red flowers dissolves in alcohol and in water without perceptibly colouring the liquid; but the addition of a few drops of acid brings out the colour: hence Filhol regards cyanin as identical with Hope's erythrogen (ii. 503).

Some red flowers, several kinds of aloe for example, contain a colouring matter dif-



ferent from cyanin, sparingly soluble in water, easily in cold alcohol, nearly insoluble in ether, and not altered in colour by acids or by bases.

All flowers contain uncrystallisable sugar (Filhol).

The statement of older observers, that the blue colours of flowers are produced from red by the action of alkalis developed in the plant, is not confirmed by experiment. Alkalis, in fact, either produce no effect on red flowers, or turn them green, but certainly not blue.

The colours of flowers are, for the most part, very fugitive, and therefore of little use in dyeing. On carthamin, the red dye obtained from the flowers of *Carthamus tinctorius*, see vol. i. p. 808.

**FLUAVIL.** A constituent of gutta percha, constituting from 4 to 6 per cent. of that substance. It is yellow, resinous, somewhat heavier than water, hard and friable at 0° C., soft at higher temperatures, pasty at 50°, liquid at 100–110°. At a stronger heat it boils and decomposes, turning brown and giving off acid vapours and hydrocarbons. It dissolves at common temperatures in alcohol (which it obstinately retains), in ether, benzene, oil of turpentine, sulphide of carbon, and chloroform, remaining as an amorphous mass when the solutions are evaporated. Sulphuric and nitric acids act upon it in the same manner as upon gutta percha; strong hydrochloric acid dissolves it without decomposition (Payen, Compt. rend. xxxv. 109). See *GUTTA PERCHA*.

**FLUCERINE.** Syn. with *FLUOCERITE*.

**FLUELLITE.** A fluoride of aluminium crystallised in minute acute rhombic octahedrons, with truncated apex, and occurring on quartz, together with wavellite and uranite, at Stanna-gwyn in Cornwall. Hardness = 3. Colour white, transparent. (Levy, Ed. J. Sci. 1825, p. 168.—Dana, ii. 98.)

**FLUOBORIC ACID.** See *BORON*, *FLUORIDE OF* (i. 633).

**FLUOCERINE.** *Basicerine.* Basic fluoride of cerium from Finbo (i. 834).

**FLUOCERITE.** *Flucrine.* Normal cerous fluoride, occurring at Finbo and Broddbo in Sweden (i. 834).

**FLUOCHLORE.** A name applied by Hermann to those varieties of pyrochlore which contain fluorine but no water. (See *PYROCHLORE*.)

**FLUOLITE.** Pitchstone from Iceland.

**FLUOR.** See *FLUOR-SPAR*.

**FLUORHYDRIC or HYDROFLUORIC ACID.** HF. This acid, which is the only known compound of fluorine and hydrogen, was first prepared, though in an impure state, containing silica, by Scheele in 1771. Gay-Lussac and Thénard, in 1808, first obtained it in the pure state, but regarded it as an oxygen-compound. Ampère, in 1810, suggested that it was a hydracid analogous to hydrochloric acid; and this view was afterwards experimentally confirmed by Davy.

*Formation and Preparation.*—Hydrofluoric acid is produced by the action of sulphuric acid on metallic fluorides, fluor-spar, which is a fluoride of calcium, being almost always used for its preparation:



To obtain the acid pure, a leaden or platinum vessel must be used, as it corrodes glass or earthenware with great rapidity. To prepare the aqueous acid in its strongest form, fluor-spar perfectly dry is mixed with twice its weight of strong sulphuric acid (specific gravity 1·85), in a leaden retort (*fig. 483*) having a bent leaden tube adapted to it, the lower part of which is immersed in a freezing mixture. The joints are made secure with clay-lister secured with a band of paper. No tin solder must be used in the construction of the apparatus, as the acid attacks tin rapidly. On applying a gentle heat, hydrofluoric acid is given off in vapour, and passing into the bent tube is there condensed into a liquid.

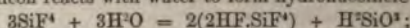
The acid thus prepared contains water, from which it may be freed by distillation with phosphoric anhydride; it is then obtained as a gas (Louyet, Compt. rend. xxii. 960); according to Frémy, however, the dehydration effected in this manner is not complete. A better mode of obtaining the dry gas is to ignite the double fluoride of hydrogen and potassium, which then splits up into its component fluorides, KF and HF. The gas may also be obtained by passing dry hydrogen over ignited fluoride of lead or other metallic fluorides.

*Fig. 483.*





Hydrofluoric acid also results from the decomposition of certain fluorides by water. Thus fluoride of silicon reacts with water to form hydrofluosilicic and silicic acids:



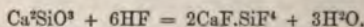
and the hydrofluosilicic acid gradually breaks up into fluoride of silicon, which evaporates, and hydrofluoric acid, which remains in solution.

Hydrofluoric gas is colourless, has a strong acid reaction, fumes in moist air, and is rapidly absorbed by water. When absolutely dry, it has but little reaction on glass. According to Frémy, it condenses at  $-20^\circ\text{C}$ . into a very mobile liquid, which reacts violently with water, forms white fumes in the air, and attacks glass readily. The concentrated aqueous acid is a colourless mobile liquid, which boils at  $15^\circ\text{C}$ .; the fumes are highly caustic and irritating, and the liquid itself is a most virulent caustic, a single drop producing a painful ulcer very difficult to heal. Its union with excess of water is accompanied by a hissing noise and a considerable development of heat. The most concentrated acid has a sp. gr. 1.06. The acid of greatest density, namely, 1.15, is more dilute, and is usually regarded as a definite hydrate,  $\text{HF}.\text{H}_2\text{O}$ , containing 35.9 p.c. HF, boiling at  $120^\circ\text{C}$ ., and distilling unchanged under the ordinary atmospheric pressure. According to Roscoe, however (Chem. Soc. Qu. J. xiii. 162), no definite hydrate of hydrofluoric acid exists, a weaker or stronger acid giving off water or hydrofluoric acid when boiled, till the residue contains from 36 to 38 p.c. HF. By leaving the aqueous acid of any strength to evaporate over quick lime at common temperatures, a residue is obtained containing 32.5 p.c. HF.

From the analogy of hydrofluoric acid to hydrochloric, hydrobromic, and hydriodic acid, it is supposed to contain equal volumes of fluorine and hydrogen gases united without condensation, its composition being therefore 1 pt. hydrogen united with 19 pts. fluorine and its atomic weight 20. This composition by volume has not, however, been determined directly: for fluorine itself has not been isolated in a satisfactory manner, and even the specific gravity of hydrofluoric acid gas is unknown.

**Reactions.**—Hydrofluoric acid acts with energy on many elementary bodies, especially the *metals*, dissolving them with evolution of hydrogen, and sometimes, as in the case of *potassium*, with explosion, and forming a fluoride. It acts in this manner, not only on the metals which are dissolved by hydrochloric acid, but likewise on those which that acid does not attack, *copper* and *silver* for example. It also dissolves many elementary bodies which are insoluble in all other acids, namely, *silicon*, *boron*, *zirconium*, *titanium* and *tantalum*, giving off hydrogen, and forming a compound of the resulting fluoride with hydrofluoric acid; with silicon (unignited), for example, it forms hydrofluosilicic acid,  $2\text{HF}.\text{SiF}^4$ . Ignited silicon and titanium are not attacked by hydrofluoric acid alone, but dissolve in a mixture of hydrofluoric and nitric acids with evolution of nitric oxide. *Gold* and *platinum*, on the other hand, are not attacked, either by the pure acid or by its mixture with nitric acid.

*Silica* and the *silicates* are very energetically attacked by hydrofluoric acid. Silica dissolves in it with great rise of temperature, forming a colourless solution of hydrofluosilicic acid,  $2\text{HF}.\text{SiF}^4$  or  $\text{H}^2\text{SiF}^6$ ; if the hydrofluoric acid is concentrated, the liquid boils and fluoride of silicon escapes as gas. With silicates it forms water, fluoride of silicon, and a metallic fluoride which unites with the fluoride of silicon; e.g. with silicate of calcium:



With silicates of different composition, an excess of metallic fluoride or of fluoride of silicon is formed, which unites with the hydrofluoric acid.

On this reaction depends the use of hydrofluoric acid for the decomposition of silicates in mineral analysis (see **SILICATES**), and for etching on glass. For the latter purpose, the glass is covered with etching wax; the design is traced upon it with a pointed instrument; and the glass is either exposed to the vapour of the acid, or the aqueous acid is poured upon it. The vapour is preferable to the liquid in this respect, that the lines which it forms on the glass are opaque, whereas those formed by the liquid are transparent and not so easily seen. Etching with hydrofluoric acid vapour is the best mode of marking scales of equal parts on glass tubes and jars.

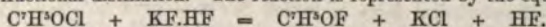
#### **FLUORIDE OF ALUMINIUM.** (i. 157.)

**FLUORIDE OF AMMONIUM.**  $\text{NH}^4\text{F}$ . This salt crystallises from a solution of hydrofluoric acid saturated with ammonia and left to evaporate over quick lime, in thin hexagonal laminae, or very brittle hollow hexagonal prisms; the crystals are somewhat deliquescent.—*Fluoride of Ammonium and Hydrogen, or Acid fluoride of ammonium*,  $\text{NH}^4\text{F}.\text{HF}$ , forms slightly deliquescent rhombic crystals of  $91^\circ 50'$ , with the terminal faces *oP*, and frequently also with the prismatic edges truncated: it is not isomorphous with the corresponding potassium-salt. (Marignac, Ann. Ch. Pharm. exi. 380.)

**FLUORIDE OF ANTIMONY.** See **ANTIMONY, FLUORIDE OF** (i. 322).

**FLUORIDE OF ARSENIC.** See ARSENIC, FLUORIDE OF (i. 371).

**FLUORIDE OF BENZOYL.**  $C^H^O.F$ . (Borodine, Cimento, xv. 305; Rép. Chim. pure, 1862, p. 336.)—Obtained by mixing in a platinum retort 1 at. chloride of benzoyl and rather more than 1 at. acid fluoride of potassium, distilling as soon as vapours of hydrofluoric acid cease to go off, and collecting in a small platinum receiver the portion which distils between  $155^{\circ}$  and  $160^{\circ}$ .\* The product may be further purified by fractional distillation. The reaction is represented by the equation:



Fluoride of benzoyl is a colourless oily liquid, heavier than water, and having an odour even more irritating than that of the chloride. It boils at  $161.5^{\circ}$  (corrected) under a pressure of 745 mm. When pure, it scarcely attacks glass; nevertheless its vapour-density cannot be taken in glass vessels. It dissolves without decomposition in ether; is converted by water into benzoic and hydrofluoric acids; forms with *potash* benzoate and fluoride of potassium; with *alcohol*, benzoic ether, and with *ammonia*, benzamide. It does not appear to unite with metallic fluorides.

**FLUORIDE OF BARIUM.** See BARIUM, FLUORIDE OF (i. 504).

**FLUORIDE OF BORON.** See BORON, FLUORIDE OF (i. 632).

**FLUORIDES OF CADMIUM, CALCIUM, CERIUM, COBALT, COPPER, &c.** See the several metals.

**FLUORIDE OF ETHYL.** See ETHYL, FLUORIDE OF (ii. 533).

**FLUORIDE OF HYDROGEN.** See FLUORHYDRIC ACID (ii. 669).

**FLUORIDE OF PHOSPHORUS.** See PHOSPHORUS, FLUORIDE OF.

**FLUORIDE OF SILICON.** See SILICON, FLUORIDE OF.

**FLUORIDES, METALLIC.** These compounds are formed: 1. By heating hydrofluoric acid with certain metals.—2. By the action of that acid on metallic oxides or carbonates.—3. By heating electro-negative metals, antimony for example, with fluoride of lead or fluoride of mercury.—4. Volatile metallic fluorides may be prepared by heating fluor-spar with sulphuric acid and the oxide of the metal.—5. Insoluble fluorides, such as fluoride of calcium may be formed by precipitation.

Fluorides have no metallic lustre; most of them are easily fusible, and for the most part resemble the chlorides. When dry, they are not decomposed by ignition, either alone or when mixed with charcoal; but when ignited in contact with the air, in a flame which contains aqueous vapour, many of them are converted into oxides, while the fluorine is given off as hydrofluoric acid. All fluorides are decomposed by *chlorine* and converted into chlorides. They are not decomposed by *phosphoric anhydride*, unless silica is present. They are decomposed at a gentle heat by strong *sulphuric acid*, with formation of a metallic sulphate and evolution of hydrofluoric acid.

The fluorides of tin and silver are easily soluble in water; those of potassium, sodium, and iron are sparingly soluble; those of strontium and cadmium very slightly soluble, and the rest insoluble. The solutions of fluoride of ammonium, potassium, and sodium have an alkaline reaction. The aqueous solutions of fluorides corrode glass vessels in which they are kept or evaporated. They form with soluble calcium-salts a precipitate of fluoride of calcium, in the form of a transparent jelly which is scarcely visible, because its refractive power is nearly the same as that of the liquid; the addition of ammonia makes it plainer. This precipitate, if it does not contain silica, dissolves with difficulty in hydrochloric or nitric acid, and is reprecipitated by ammonia. The aqueous fluorides give a pulverulent precipitate with acetate of lead.

The fluorides of antimony, arsenic, chromium, mercury, niobium, osmium, tantalum, tin, titanium, tungsten, and zinc, are volatile without decomposition.

**Double Fluorides.**—Fluorine has a great tendency to form double salts, consisting of a fluoride of a basic or positive metal united with the fluoride of hydrogen, boron, silicon, tin, titanium, zirconium, &c., e.g.:

Fluorhydrate of potassium	. . . . .	$KHF^2 = KF.HF.$
Borofluoride of potassium	. . . . .	$KBF^4 = KF.BF^3.$
Silicofluoride of potassium	. . . . .	$K^2SiF^6 = 2KF.SiF^4.$
Titanofluoride of potassium	. . . . .	$K^2TiF^6 = 2KF.TiF^4.$
Stannofluoride of potassium	. . . . .	$K^2SnF^6 = 2KF.SnF^4.$
Zirconofluoride of potassium	. . . . .	$K^2ZrF^6 = 2KF.ZrF^4.$

It will be observed that the double fluorides of silicon, titanium, tin, and zirconium are represented by corresponding formulæ. It appears indeed from the experiments of Marignac (Ann. Ch. Pharm. cvii. 94; cxi. 380; cxvi. 359.—Ann. Ch. Phys.

\* The tube of the thermometer should be protected by placing it within a small tube of platinum passing through the tubulure of the retort.



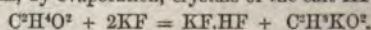
[3] *lx.* 257.—*Jahresber. d. Chem.* 1858, p. 144; 1859, p. 106; 1860, p. 134), that the corresponding double fluorides of silicon, tin, and titanium crystallise for the most part with the same number of atoms of water, and are isomorphous with each other. Thus the silicofluorides and stannofluorides of strontium crystallise each with 1 at. water, have nearly the same degree of solubility in water, and form monoclinic crystals in which  $\alpha P : \alpha P$  is, in the former,  $= 84^\circ 16'$ , in the latter,  $= 82^\circ 23'$ . The zinc-fluorides of tin and silicon crystallise with 3 at. water in hexagonal prisms with rhombohedral faces, in which  $R : R = 127^\circ 16'$ , and similar forms are exhibited by the corresponding salts of nickel ( $R : R = 127^\circ 30'$ ) and cadmium ( $R : R$  for the stannofluoride  $= 127^\circ$ ). The corresponding salts of cobalt, iron, manganese, and copper are likewise isomorphous with the preceding, and agree with them in their optical properties. The zirconfluorides or fluozirconates exhibit isomorphism with the corresponding silicofluorides, &c., in a few cases, but by no means in all.

The great tendency of fluorine to form double salts, has led to the idea that it should be regarded as diatomic and analogous to oxygen, with the atomic weight 38, rather than as monatomic and analogous to chlorine, with the atomic weight 19. On this supposition, denoting the larger atom of fluorine by  $Ff$ , the formulæ of the fluorides would be as follows:

Hydrofluoric acid . . . . .	$= \frac{H}{H} \left\{ Ff \right.$
Fluoride of potassium and hydrogen . . . . .	$= \frac{H}{K} \left\{ Ff \right.$
Fluoride of potassium . . . . .	$= \frac{K}{K} \left\{ Ff \right.$
Fluoride of boron . . . . .	$= B^2 Ff.$
Borofluoride of potassium . . . . .	$= \frac{K}{B} \left\{ Ff \right.$
Fluoride of silicon . . . . .	$= Si Ff.$
Silicofluoride of potassium . . . . .	$= \frac{K^2}{Si} \left\{ Ff \right.$

The question cannot be directly decided, because, as already observed, the vapour-densities of fluorine and of hydrofluoric acid are not known; but the recent experiments of Borodine (*Cimento*, xv. 305; *Rép. Chim. pure*, 1862, p. 334) tend strongly to the conclusion that fluorine is monatomic, as hitherto supposed, and that the double fluorides are analogous to the double chlorides, iodides, &c., rather than to the double sulphides and oxides, or to the double salts of dibasic acids.

The fluorides of potassium and sodium have a great tendency to unite with hydrofluoric acid, and form acid fluorides, and consequently they readily give up half their metal even to the weakest acids. Thus a solution of fluoride of potassium mixed with dilute acetic acid yields, by evaporation, crystals of the salt  $KF.HF$ :



A similar action takes place with fluoride of sodium.

An aqueous solution of benzoic acid does not act on fluoride of potassium; but an alcoholic solution of that acid mixed with the aqueous solution of the fluoride yields a crystalline precipitate, which is a mixture of acid benzoate and acid fluoride of potassium,  $C^2H^4KO^2.C^2H^4O^2 + KF.HF$ . A similar action is exerted by valeric, citric, oxalic, and tartaric acids. Hence it appears that all organic acids decompose the fluorides of potassium, or of sodium, forming an acid fluoride, but do not themselves unite with the alkaline fluoride in the same manner as hydrofluoric acid does.

**FLUORIDES, ORGANIC.** Only a few compounds of fluorine with organic radicles have been obtained, viz. the fluorides of *benzoyl* (p. 671), *ethyl* (p. 533), and *methyl* (q. v.).

**FLUORINE.** Atomic weight, 19; symbol,  $F$ . This element is widely diffused, but not in large quantities. It occurs most abundantly as fluoride of calcium, and is also found in fluoride of cerium, topaz, cryolite, warwickite, and yttrocerite; and in small quantity in fluor-apatite, wagnerite, amblygonite, wavellite, and many other minerals. It also occurs in bones and teeth, both recent and fossil, and in urine. Professor Wilson, of Edinburgh, has shown that fluorine exists in a great number of plants, especially in the siliceous stems of grasses and equisetaceous plants, always, however, in very small and variable quantities. He supposes that soluble fluorine compounds diffuse themselves through the rising sap of the plant, and are converted, by the silica contained therein, into soluble silico-fluorides. Traces of fluorine also occur in the trap-rocks near Edinburgh and in the neighbourhood of the



Clyde, in the granites of Aberdeenshire, and in the soils formed by the disintegration of those rocks. Wilson has also found slight traces of fluorine in the ashes of ox-blood, milk, and cream-cheese, and very slight traces in the ash of the whey of milk. (Edin. Phil. J. liii. 356; Chem. Gaz. 1850, p. 366.)

Small quantities of fluorine have been found in the waters of the Seine, Rhone, Saone, Loire, and other rivers (Nicklès, *Compt. rend.* xlv. 783; xlv. 331. *Mène, ibid.* l. 731), and in larger quantity in certain mineral waters, especially those of Contrexéville, Antogast, and Châtenois. (Nicklès.)

According to Nicklès, fluoride of calcium occurs in all waters which contain acid carbonate of calcium, and may therefore be found in all calcareous rocks and minerals formed by sedimentary deposition.

Of fluorine in the free state we know but little. Fluorides are decomposed by chlorine and converted into chlorides, and doubtless the fluorine is at the same time set free; but it directly enters into combination with the material of almost every vessel that can be used to receive it, so that its isolation is a matter of great difficulty.

Louyet (*Compt. rend.* xxii. 960) decomposed fluoride of silver by means of chlorine or iodine in a vessel made of fluor-spar, and obtained a gas which was colourless in thin strata, did not bleach vegetable colours, decomposed water rapidly, and attacked most metals, not however, gold or platinum. Frémy (*Compt. rend.* xxxviii. 393; xl. 966), by submitting fused fluoride of potassium to the action of the voltaic current, obtained a gas which rapidly attacked platinum, decomposed water, with formation of hydrofluoric acid, and displaced iodine from its combinations with metals. By decomposing fluoride of calcium at a red heat with dry chlorine or oxygen, he likewise obtained a gas which rapidly attacked glass: this gas appeared to be fluorine.

H. Reinsch (*N. Jahrb. Pharm.* xi. 1), by heating a mixture of eryolite, peroxide of lead, and acid sulphate of potassium, obtained a colourless gas, chiefly consisting of oxygen, but having a pungent odour, like that of nitrous acid, which he attributed to the presence of a small quantity of free fluorine.

Kämmerer (*J. pr. Chem.* lxxxv. 452), by heating iodine with excess of fluoride of silver in a sealed tube, from which the air had been expelled by iodine-vapour, obtained a colourless gas, which did not attack glass, could be collected over mercury, and was rapidly absorbed by potash, the liquid subsequently not exhibiting a trace of iodine or of silicon.

#### FLUORINE, DETECTION AND ESTIMATION OF. 1. *Reactions.*—

Fluorine is usually detected by the evolution of hydrochloric acid which takes place when its compounds are heated with sulphuric acid. When a fluoride is gently heated with strong sulphuric acid in a leaden cup or platinum crucible; the vessel covered with a plate of glass coated with etching-wax on which lines are traced with a needle, so as to expose the surface of the glass, the plate removed after a while, and the wax scraped off; the lines are found to be bitten in, and appear particularly distinct when breathed upon.

If the fluorine is in very small quantity, or if silica is likewise present, the substance under examination should be mixed with strong sulphuric acid in a watch-glass, heated till it is dry, and the residue washed off with water; the spot on which the mixture has been evaporated then appears dull. Another method of detecting small quantities of fluorine, is to heat the substance (mixed with silica if that body is not already present) with strong sulphuric acid in a glass vessel; pass the evolved fluoride of silicon into water; supersaturate the resulting hydrofluosilicic acid with ammonia; evaporate to dryness; exhaust the residue with water; again evaporate the filtrate; and test the residue in the ordinary way, by heating it with sulphuric acid in a platinum vessel covered with a waxed glass plate. (G. Wilson, *Chem. Soc. Qu. J. v.* 151.)

Nicklès (*Compt. rend.* xlv. 679) points out that in searching for traces of fluorine, error is very apt to arise from the presence of small quantities of hydrofluoric acid in the sulphuric acid used; also from the fact that certain other acids in the state of vapour act upon glass in a similar manner to hydrofluoric acid, though not so powerfully. He states that a surface of rock-crystal completely withstands the action of all acids except hydrofluoric acid, and that by using it instead of glass, the minutest traces of fluorine may be detected with certainty.

Small quantities of fluorine may also be detected by the blow-pipe, especially if the substance examined likewise contains water. A sample is intimately mixed with microcosmic salt, and heated at the end of a glass tube open at both ends, in such a manner that the flame may be partly driven into the tube. If fluorine is present, hydrofluoric acid is given off, and condenses, together with vapour of water, in the upper and cooler part of the tube; on evaporating the water, a dull spot is found where the hydrofluoric acid has acted on the glass.

2. *Quantitative estimation.*—Solid fluorides are decomposed by heating them in a platinum crucible with strong sulphuric acid, continuing the heat till all the fluorine is expelled in the form of hydrofluoric acid, and the excess of sulphuric acid is likewise drawn off. The residual sulphate is then weighed, and the quantity of metal in it calculated; this quantity deducted from the original weight of the fluoride gives the quantity of fluorine. Or, supposing no other volatile acid to be present, if the difference in the weight of the fluoride and the sulphate formed from it be  $d$ , the quantity of the fluorine may be found by means of the equations,

$$\text{SO}^4 - \text{F}^2 = d; \quad \frac{\text{SO}^4}{\text{F}^2} = \frac{48}{19};$$

whence the quantity of fluorine which goes off is

$$\text{F}^2 = \frac{19}{48-19} d = \frac{19}{29} d.$$

The second mode of calculation is equally applicable, whether the fluorine be combined with one metal or with several.

Some fluorides, especially the fluoride of aluminium, are somewhat difficult to decompose by sulphuric acid. In this case, the substance must be reduced to extremely fine powder, and heated for some time with very strong sulphuric acid. The decomposition may, however, be more quickly effected by fusion with *acid sulphate of ammonium*. When fluoride of aluminium is thus treated, and the residual sulphate of aluminium calcined with addition of a small quantity of carbonate of ammonium, a residue of pure alumina is obtained; and by calculating the quantity of aluminium contained therein, the amount of fluorine may be determined by difference; if, however, the fluoride contains water, the amount of the water must be previously determined.

In decomposing fluorides by sulphuric acid, it is often desirable to estimate the amount of fluorine directly. For this purpose, the acid vapours evolved are passed into water, and the amount of fluorine is determined by means of oxide of lead, as will be presently explained.

As gaseous fluoride of silicon is more easily separated from solid compounds by the action of strong sulphuric acid than hydrofluoric acid, Wöhler has proposed to determine the fluorine in certain compounds by mixing them with *silica*, and treating them with strong sulphuric acid. The fluorine is then given off as fluoride of silicon, which, when passed into water, is resolved into a precipitate of silica and a solution of hydrofluosilicic acid. The liquid separated from the silica by filtration is mixed with alcohol and with a salt of potassium, sodium, or barium, whereby a precipitate is formed containing the whole of the fluorine in the form of silicofluoride of potassium, sodium, or barium; this precipitate is collected on a weighed filter, washed with a mixture of equal volumes of alcohol and water, dried at  $100^\circ \text{C}$ . and weighed, and the amount of fluorine determined from it by calculation.

*Estimation of Fluorine in Solutions: a. By means of Oxide of Lead.*—In a liquid containing hydrofluoric acid, unmixed with any base, or with any acid except nitric acid, the quantity of fluorine may be determined by adding a weighed quantity of pure calcined oxide of lead, evaporating to dryness in a platinum capsule, and calcining the residue in a small platinum crucible, taking care not to raise the heat high enough to decompose the fluoride of lead. The solution must not contain ammonia or any of its salts. The residue exhibits an increase of weight, arising from the substitution of fluorine for oxygen; and a calculation similar to the above shows, that *this increase is to the quantity of fluorine in the residue, in the same ratio as the difference between the atomic weight of fluorine and half the atomic weight of oxygen is to the atomic weight of fluorine*. Hence if the increase of weight be  $d$ , the quantity of fluorine in the residue is

$$f = \frac{19}{19-8} d = \frac{19}{11} d.$$

*b. By precipitation as Fluoride of Calcium.*—In neutral liquids containing soluble fluorides, the fluorine may be precipitated by chloride of calcium. To facilitate the deposition of the precipitate, the whole must be boiled, and left to itself for the precipitate to settle down; the clear liquid then poured through a filter; the remaining precipitate well boiled with water; the clear liquid again poured off; and these operations repeated several times, the precipitate not being poured upon the filter till it has been well washed by decantation. It is then dried, ignited, and weighed. It contains 48.32 per cent. of fluorine.

If the solution is acid, it is best to supersaturate it with carbonate of sodium, and add a solution of chloride or nitrate of calcium, which throws down a mixture of fluoride and carbonate of calcium, much easier to filter and wash than the fluoride alone. It is dried and ignited, the filter being burnt in the ordinary way; then digested in a platinum capsule with acetic acid, which decomposes and dissolves



the carbonate of calcium, but leaves the fluoride untouched. The whole is evaporated to dryness over the water-bath, till the residue no longer smells of acetic acid; and this residue is tested with hot water, which dissolves the acetate of calcium, leaving the fluoride, which may be washed, dried, and weighed as above. If the precipitate were not calcined before being treated with acetic acid, it would stop up the pores of the filter during washing.

If the solution of a fluoride contains ammoniacal salts, they must be decomposed by boiling with carbonate of sodium before precipitation, inasmuch as fluoride of calcium is somewhat soluble in ammonia-salts.

Fluorine may also be precipitated as *fluoride of barium*, or of *lead*; but these modes of estimation are less exact than that which is based on the precipitation by calcium salts as just described.

*Estimation of Fluorine in insoluble compounds.*—When the quantity of fluorine in an insoluble compound is somewhat considerable, the method of estimation by decomposition with sulphuric acid (p. 674) is the simplest and most accurate that can be employed; but very small quantities of fluorine cannot be exactly estimated in this manner. The best mode of proceeding in such cases, is to convert the insoluble fluoride into a soluble fluoride by fusion with an *alkaline carbonate*, treat the fused mass with water, and precipitate the filtered solution with chloride or nitrate of calcium in the manner already described. Some of the earthy fluorides, however, especially fluoride of calcium, which is of frequent occurrence as a natural mineral, cannot be completely decomposed by this process. In all cases, however, complete decomposition may be effected by fusing the fluoride with a mixture of *alkaline carbonate and silica*; fluoride of calcium thus treated yields a mixture of alkaline fluoride and silicate, with carbonate and silicate of calcium. On treating the fused mass with water, a solution is obtained containing a fluoride of the alkali-metal, together with carbonate and a small quantity of silicate. The silica may be precipitated as silicate of zinc, by adding to the alkaline liquid a solution of zinc in ammonia; and from the filtrate, which contains fluoride and carbonate of the alkali-metal, the fluorine may be precipitated by a calcium-salt, and the estimation completed in the manner already described.

*Estimation of free Hydrofluoric acid in presence of Fluorides.*—In compounds of metallic fluorides with hydrofluoric acid, the amount of the latter may often be estimated by simple calcination in a platinum crucible. In some cases, however, the residual metallic fluoride is partly decomposed by contact with the air. To avoid the source of error thence arising, Berzelius mixed the compound with six times its weight of oxide of lead, and calcined the whole in a small retort. The free hydrofluoric acid is then decomposed, yielding fluoride of lead and water, which escapes and may be estimated by loss, and the equivalent quantity of hydrofluoric acid thence determined. Another portion of the compound is decomposed by sulphuric acid (p. 674); the quantity of fluorine existing in the compound as metallic fluoride is determined from the amount of sulphate thus obtained; and this, added to the quantity present as hydrofluoric acid, gives the total quantity of fluorine in the compound.

If the compound likewise contains water of crystallisation, the loss of weight resulting from calcination with oxide of lead represents the sum of this water of crystallisation, and the water which is formed by combination of the hydrogen of the hydrofluoric acid with the oxygen of the lead-oxide. The total quantity of fluorine originally in combination with the metal, may then be determined by heating the calcined residue with sulphuric acid; and this diminished by the quantity originally in combination with the metal,—which may be determined by heating a separate portion of the original substance with sulphuric acid, as above,—gives the quantity present as hydrofluoric acid. The amount of water equivalent to this latter quantity may then be calculated, and this deducted from the loss of weight resulting from calcination with lead-oxide, gives the amount of water of crystallisation.

3. *Separation of Fluorine from other elements.*—1. From *Metals*. Fluorides soluble in water or in acids may, in many cases, be decomposed by precipitating the metal as sulphide with sulphydric acid. The filtered liquid is then saturated with carbonate of sodium, and the fluorine precipitated by chloride of calcium. If the solution is acid, the precipitation of the metal must be performed in a platinum vessel (since free hydrofluoric acid attacks glass), and the liquid filtered on a platinum funnel; or the solution may be supersaturated with the alkaline carbonate; the precipitate decomposed, without previous filtration, by sulphuric acid: the liquid then filtered, and the fluorine precipitated by chloride of calcium: by proceeding in this manner, the whole process may be performed in glass vessels.

Compounds of fluorine with metals which are not precipitated by sulphydric acid as sulphides, viz. the fluorides of the earth-metals, cannot be decomposed in this manner, but must be treated either with sulphuric acid (p. 674), or by fusion with carbonate of sodium and silica.



From *Chromic acid*.—When a solution containing hydrofluoric and chromic acids, is treated with chloride of calcium, a small quantity of chromic acid is always precipitated together with the fluoride of calcium, and consequently exhibits a green colour after calcination, the chromic acid having been partly reduced to sesquioxide by the combustion of the filter. To separate this small quantity of chromium, the calcined precipitate is moistened with sulphuric acid, which decomposes it completely, and the decomposed mass is heated with alcohol diluted with half its bulk of water, and the resulting sulphate of calcium is washed with alcohol. The filtered solution, which contains all the chromium in the form of chromic sulphate, is treated with ammonia, which precipitates the chromium in the form of sesquioxide.

The liquid filtered from the original precipitate of fluoride of calcium contains the greater part of the chromium in the form of chromate of calcium. The chromic acid is reduced to sesquioxide by means of hydrochloric acid and sulphydric acid or alcohol, and the chromium precipitated by ammonia from the filtrate as sesquioxide. From this quantity, added to the small quantity previously determined, the amount of chromic acid or metallic chromium in the compound may be found by calculation.

The quantity of chromate of calcium equivalent to the sesquioxide of chromium separated from the fluoride of calcium, must also be determined; and this deducted from the total weight of the calcined precipitate, gives the exact quantity of the fluoride of calcium. This method may serve for the analysis of fluoride of chromium (i. 946).

For the separation of fluorine from *Boron* see i. 631.

*Separation of Fluorides from Phosphates*.—Fluorides frequently occur in nature in conjunction with phosphates, as in apatite and in bones. To analyse such a compound, it is first heated with sulphuric acid, to expel the fluorine; the residue digested with alcohol to dissolve the phosphoric acid which has been set free; the quantity of that acid determined by precipitation with ammonia and sulphate of magnesium; and the metals, now remaining in the form of sulphates, determined by the usual methods. Lastly, the total weight of these metals, together with that of the phosphoric acid, or rather of the corresponding salt-radicle ( $\text{PO}_4$ , if the phosphates are tribasic) is deducted from the original weight of the mineral; and the difference gives the quantity of fluorine.

For the separation of fluorides from *silicates*, see *SILICON, ESTIMATION OF*.

*Separation of Fluorides from Sulphates*.—Some fluorides occur in nature mixed with insoluble sulphates; fluor-spar with sulphate of barium for example. Such a mixture cannot be completely decomposed, either by hydrochloric acid, or by alkaline carbonates: for hydrochloric acid, besides dissolving a small quantity of the sulphate, leaves a portion of the fluoride of calcium mixed with the undissolved sulphate; and fusion with alkaline carbonates decomposes the sulphate of barium completely, but not the fluoride of calcium. The only way of effecting the complete decomposition of such a mixture is to fuse it with a mixture of alkaline carbonate and silica; best with six times its weight of a mixture of potassic and sodic carbonates in atomic proportions, and 2 pts. of silica.

The fused mass is treated with water, the whole evaporated to dryness to separate the silica as completely as possible, the alkaline liquid then supersaturated with hydrochloric acid, and precipitated by chloride of barium. Sulphate of barium is thereby precipitated quite free from fluorine: this determines the sulphuric acid.

To determine the fluorine, the alkaline liquid from another portion must be supersaturated with nitric acid, the sulphuric acid precipitated by nitrate of barium, the filtrate exactly saturated with carbonate of sodium, and the fluorine precipitated as fluoride of barium by addition of alcohol.

The residue insoluble in water is treated with hydrochloric acid; the whole is evaporated to dryness, the dried mass moistened with hydrochloric acid, and boiled with water to separate silica, and the baryta and lime separated in the filtrate by methods already given (i. 717).

*Separation of Fluorine from Chlorine*.—In neutral soluble compounds, chlorine may be separated from fluorine by precipitation with nitrate of silver. The excess of silver is then separated by hydrochloric acid, the filtrate saturated with carbonate of sodium, and the fluoride precipitated as fluoride of calcium.

Or the fluorine may be first precipitated by nitrate of calcium, and the chlorine from the filtrate by nitrate of silver. This is the easier method of the two.

To effect the separation of chlorine and fluorine in insoluble compounds, it is in most cases necessary to decompose the compound with a mixture of alkaline carbonate and silica. The fused mass is then treated with water, which dissolves the chloride and fluoride of the alkali-metal, together with the excess of the alkaline carbonate, and a small quantity of silica. The residue is washed with water containing carbonate of ammonia, and the alkaline filtrate is exactly neutralised with nitric acid to separate the dissolved silica, the liquid again filtered, and the chlorine and fluorine separated as above.

Similar methods may be used to separate fluorine from *bromine* and *iodine*.

4. *Atomic weight of Fluorine.*—Berzelius (Pogg. Ann. i. 1; Lehrb. 5<sup>te</sup> Aufl. iii. 1196) determined the atomic weight of fluorine by converting known weights of fluoride of calcium into sulphate, by decomposing it with pure sulphuric acid, and igniting and weighing the product.

100 pts. of Derbyshire fluor-spar gave, when thus treated, from 173.63 to 173.86 pts. sulphate of calcium. The material used for these experiments was, however, afterwards found to contain phosphoric acid and magnesia, so that the following determinations, made with artificially prepared fluoride of calcium, may be considered more accurate. 100 pts. of the latter material gave—174.9, 175.0, and 175.1, on the average 175.0 pts. sulphate of calcium. Taking Ca = 20, S = 32, and O = 16, these results lead to the number 18.85 for the atomic weight of fluorine. Berzelius, however, considered this number as still only approximately correct.

Louyet (Ann. Ch. Pharm. lxx. 234), on repeating the determination in the same way, got nearly similar results. 100 pts. of almost colourless Derbyshire fluor-spar gave him from 173.5 to 173.6 pts. sulphate of calcium; mean 173.63 pts. Artificial fluoride of calcium gave 173.4, 173.5, and 173.7 pts. sulphate of calcium. The mean of these analyses gives 19.2 as the atomic weight of fluorine.

Louyet observed, however, that the complete decomposition of fluor-spar by sulphuric acid, took place only with great difficulty. Finally, he succeeded in effecting it by pulverising the fluor-spar very finely, treating it in the cold with concentrated sulphuric acid, heating the mixture when the spar was entirely dissolved, and then strongly igniting the residue. Six experiments made in this way gave from 174.2 to 174.6 pts. sulphate from 100 pts. of fluoride of calcium. The atomic weight of fluorine hence deduced is 19.0. Experiments with artificial fluorides of calcium, barium, and lead, confirmed this result (Handwörterb. 2<sup>te</sup> Aufl. ii. [1] 485). Dumas' experiments on the decomposition of native fluoride of calcium, and of the artificially prepared fluorides of potassium and sodium by sulphuric acid, also gave for fluorine the number 19 (Ann. Ch. Pharm. cxiii. 20).

**FLUOR-SPAR.** CaF. *Fluor. Fluorite. Fluoride of Calcium. Fluat of Lime. Ratoffkite. Chlorophane. Blue John. Liparite. Chaux fluatée. Fluss-spath. Muria phosphorans.*—This mineral crystallises in simple forms of the monometric system; viz. the cube, octahedron, rhombic dodecahedron, tetrakis-hexahedron  $30\infty$  (like fig. 484, which represents  $20\infty$ ), &c.; also in combinations of the cube and

Fig. 484.

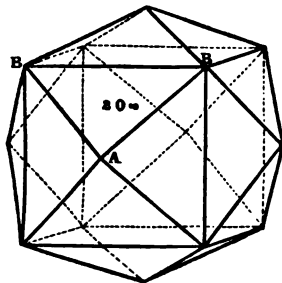


Fig. 485.

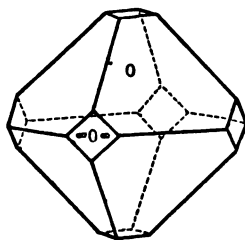


Fig. 486.

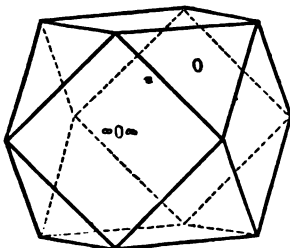
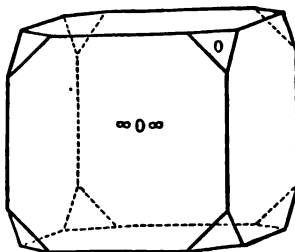


Fig. 487.



octahedron (figs. 485, 486, 487); also  $O \cdot \infty O$  (fig. 488);  $\infty O \infty \cdot \infty O$  (fig. 489);  $\infty O \infty \cdot 202$  (fig. 490);  $\infty O \infty \cdot 30\infty$  (fig. 491) and  $\infty O \infty \cdot 204$  (fig. 492).

Twin-crystals occur formed by the intersection of two equal cubes (fig. 493), having

a diagonal in common, and one turned round  $180^\circ$  from the position of the other; more frequently, however, the intersection is not quite so regular, the cubes either being of different sizes, or having their diagonals parallel, but not exactly coincident. Cleavage, octahedral perfect (*Kopp's Krystallographie*, p. 122).—Fluor-spar also occurs columnar, though rarely; often granular, coarse or fine.

Hardness = 4. Specific gravity 3.14 — 3.19, or according to Kenngott, from examination of 48 specimens, 3.1800 — 3.1889, mean 3.183.

Fluor-spar is transparent to subtranslucent, and has a glassy, sometimes splendid lustre. It is sometimes perfectly colourless and transparent, but much more frequently

Fig. 488.

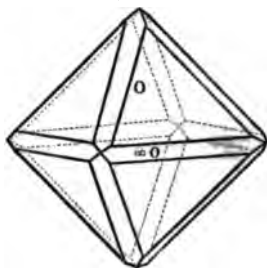


Fig. 490.

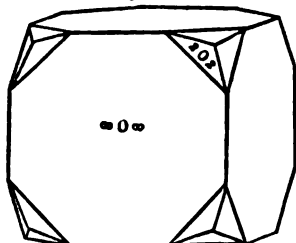


Fig. 492.

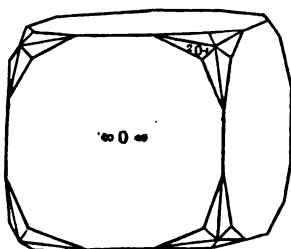


Fig. 489.

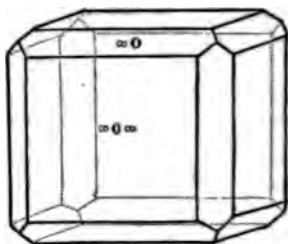


Fig. 491.

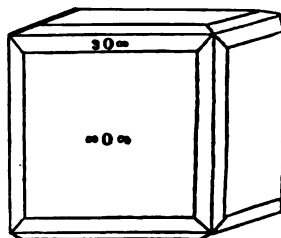
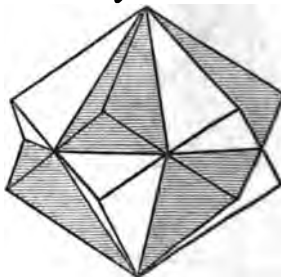


Fig. 493.



coloured, exhibiting very pure and bright tints of yellow, green, blue, and red, of the most various shades. These colours do not arise from the presence of mineral pigments, for they nearly all disappear when the mineral is heated to redness. On the other hand, it is by no means probable that they are due to the presence of organic matter; they appear rather to depend upon the molecular structure of the mineral, and to be connected with its property of exhibiting phosphorescence when heated (*Handw. d. Chem.* iii. 171). Streak white. Brittle. Fracture of fine massive varieties, flat conchoidal, and splintery.

Nearly all varieties of fluor-spar, especially in the state of powder, when heated to a temperature somewhat below redness, exhibit vivid phosphorescence, the light emitted being of various colours, and independent of the external colour. This effect may be produced several times successively with the same specimen of fluor-spar, provided the temperature be not raised above a certain limit; but above this limit the mineral completely loses its phosphorescent power, and likewise becomes colourless, a coincidence



which seems to indicate that the conditions which produce the colour and the phosphorescence are the same, or at least closely related. The phosphorescent power which has been lost by exposure to a high temperature, may be partially restored by an electric discharge.

Before the blowpipe, fluor-spar decrepitates and ultimately melts to an enamel. If the flame be continued, the fluorine is partly expelled, and the specimen assumes a cauliflower-like appearance. Easily decomposed by heating with strong sulphuric acid (p. 669).

Pure fluor-spar contains 48.7 per cent. fluorine and 51.3 calcium. The mineral generally, however, contains small quantities of phosphate of calcium, and sometimes sulphate of barium. Berzelius found 0.5 per cent. phosphate of calcium in the fluor-spar of Derbyshire. Kersten, in a fluor-spar from Marienberg and Freiberg, detected a small quantity of chlorine. The blue granular or earthy variety called Ratoffkite, from Ratoffka in Russia, is mixed with clay.

Fluor-spar is a mineral of very frequent occurrence, especially in association with metalliferous veins; as with silver, copper, tin, lead, and cobalt ores. It sometimes occurs as an unessential constituent of certain rocks, especially of some varieties of granite and porphyry, and most frequently where these rocks border on others. It occurs, however, also in distinct veins, as in the neighbourhood of Freiberg and in the Harz. In the latter district, near Stolberg, there is a very extensive vein of compact fluor-spar, which has for years supplied the Mansfeld copper works with the fluoride of calcium which they require as a flux.

In the North of England, fluor-spar forms the gangue of the lead-veins which intersect the coal-formations of Northumberland, Cumberland, Durham, and Yorkshire; the Cumberland fluor, especially the green variety, often contains drops of liquid. It is abundant in Derbyshire, and also in Cornwall, where the veins intersect much older rocks. Professor Rogers has detected it in cannel coal.

Fluor-spar is also found abundantly in many parts of North America. A remarkable locality, now exhausted, was discovered on the borders of Muscalonge Lake, in Jefferson county, New York, where cubical crystals, some of them more than a foot through, and having a greenish tinge, were found in granular limestone. *Chlorophane* forms two veins in gneiss about 18 inches wide in the town of Trumbull, Connecticut, together with topaz and magnetic pyrites.

Fluor-spar is much used as a source of hydrofluoric acid (ii. 669), and as a flux in metallurgical operations, for instance, in Deville's method of preparing aluminium (i. 150).

*Altered forms.*—Fluor-spar is slightly soluble in water containing acid carbonate of calcium. The alkaline carbonates decompose it, producing carbonate of calcium or calcespar, and a subsequent change of the calcespar may produce other pseudomorphs. Fluor-spar occurs changed to quartz by substitution, also to limonite, hæmatite, lithomarge, pailomelane, calamine, smithsonite, and cerusite. (Dana, ii. 95.)

**FLUOSILICANILIDE.** A product of the decomposition of phenylamine by fluoride of silicon. (See PHENYLAMINE, DECOMPOSITIONS.)

#### FLUOSILICATES.

#### FLUOTANTALATES.

#### FLUOTITANATES.

See FLUORIDES, also SILICON, TANTALUM, and TITANIUM.

**FLUX.** A general term for any substance or mixture added to assist the fusion of minerals. In the large way, limestone and fluor-spar are used as fluxes. The fluxes used in assays or blowpipe experiments consist usually of alkalis, which render the earthy mixtures fusible by converting them into glass, or else glass itself in powder.

Alkaline fluxes are either the *crude* flux, the *white* flux, or the *black* flux. Crude flux is a mixture of nitre and tartar, which is put into the crucible with the mineral intended to be fused. The detonation of the nitre with the inflammable matter of the tartar is of service in some operations, though generally it is attended with inconvenience, on account of the swelling of the materials, which may throw them out of the vessel, if proper care be not taken either to throw in only a little of the mixture at a time, or to provide a large vessel.

White flux is formed by projecting equal parts of a mixture of nitre and tartar, by moderate portions at a time, into an ignited crucible. The mass thus obtained is white, because, in this proportion, the oxygen of the nitre is more than sufficient for the combustion of the carbon in the tartar; but for that very reason the residue contains a considerable quantity of nitrite of potassium, and likewise some nitrate.

Black flux differs from the preceding in the proportion of its ingredients. In this, the weight of the tartar is double that of the nitre; on which account the combustion is incomplete, and a considerable portion of the tartaric acid is decomposed by the mere heat, and leaves a quantity of coal behind, on which the black colour depends.

It is used where metallic ores are intended to be reduced, and effects this purpose by combining with the oxygen of the oxide.

Morveau's reducing flux is made of eight parts of pulverised glass, one of calcined borax, and half a part of charcoal powder. Care must be taken to use a glass which contains no lead. The white glasses contain in general a large proportion, and the green bottle glasses are not entirely free from it.

Cyanide of potassium is much used as a fusing and reducing agent; when ignited with metallic oxides, it is converted into cyanate of potassium, reducing some oxides, as oxide of lead, to the metallic state; others, as peroxide of manganese, to a lower degree of oxidation (see BLOWPIPE).

**FLY-POWDER.** This term is applied to various preparations of arsenic, used for poisoning flies. (See *Ur's Dictionary of Arts, &c.*, ii. 280.)

**FODDER.** The following analyses of the ash of various fodder-plants have been made by Way and Ogston (*Roy. Agr. Soc. J. xi.* [2] 536; *Jahresber. d. Chem.* 1850, No. 76—84 of Table B, p. 661).

*Ash of Fodder-plants.*

	Medicago sativa.	Tritifolium pratense.	Tritifolium pratense, perenne.	Tritifolium medium.	Vicia sativa.	"Albena" Clover.	Plantago lanceolata.	Poterium angustiorba.	Achillea millefolium.
Potash . . . . .	9.99	36.45	22.12	34.72	32.82	29.72	33.26	30.26	30.27
Soda . . . . .			2.82						
Lime . . . . .	45.95	22.62	26.61	24.56	20.78	26.83	19.01	24.82	13.40
Magnesia . . . . .	3.60	4.08	10.22	4.52	5.31	4.01	3.51	4.21	3.01
Ferric oxide . . . . .	0.75	0.26	0.33	0.23	0.65	0.71	0.90	0.86	0.21
Sulphuric anhydride . . . . .	2.85	1.85	2.15	1.08	2.52	3.52	6.11	4.84	2.44
Silicic anhydride . . . . .	0.59	0.59	1.14	0.63	1.28	1.73	2.37	0.83	9.92
Carbonic anhydride . . . . .	26.48	23.47	22.70	25.51	18.73	20.74	14.40	21.72	9.36
Phosphoric anhydride . . . . .	5.96	6.71	8.46	5.41	10.59	5.64	7.08	7.81	7.13
Chloride of potassium . . . . .	1.54	2.39		0.85	3.27	6.29	4.53	3.27	20.49
Chloride of sodium . . . . .	1.90	1.53	3.40	2.46	4.03	1.05	8.80	1.35	3.63
Ash per cent. in dry substance . . . . .	99.61	99.95	99.95	99.97	99.98	100.24	99.97	99.97	99.96
Ash per cent. in fresh substance . . . . .	10.11	9.56	8.35	7.97	6.50	7.69	8.68	7.97	13.45
Moisture in 100 pts. of air-dried substance . . . . .	69.95	81.01	81.05	77.57	82.90	69.25	84.75	85.56	
Sulphur in 100 pts. of dry substance . . . . .	2.73	2.69	1.02	2.06	2.38	2.51	3.26	2.13	1.67

On the nutritive value of fodder, see the article NUTRITION; also the following memoirs (arranged chronologically).

On the effect of Salt added to Fodder (Boussingault, *Ann. Ch. Phys.* [3] xx. 113; xxii. 115, 503; *Jahresber. d. Chem.* 1847-8, p. 1101).

Difference between the action of Moist and Dry Fodder (E. Oppermann, *Ann. Ch. Phys.* [3] xix. 249; *Jahresber.* 1847-8, p. 1102).

Nutritive value of Fodder proportional to its amount of Nitrogen (Henneberg, *Ann. Ch. Pharm.* lxix. 336; *Jahresber.* 1849, p. 527.—Lassaigne, *Compt. rend.* xxix. 527; *Jahresber.* 1849, p. 527).—On the contrary (Völeker, *Chem. Gaz.* 1850, p. 337; *Jahresber.* 1850, p. 563).

Relation between the Composition of Fodder and the Respiration and Nutrition of animals (Lawes and Gilbert, *Reports of British Association*, 1852; *Jahresber.* 1853, p. 759).

Nutritive value of Lucern, Mulberry-leaves, and Marc of Grapes, as fodder for sheep (Marès, *Rev. scient.* [4] i. 117; *Jahresber.* 1852, p. 817).

Feeding of Merino sheep (Wolff and Bähr, *Pharm. Centr.* 1852, p. 694; *Jahresber.* 1852, p. 818).

Nutritive value of various kinds of Fodder (Anderson, *Journal of Agriculture*, No. 30, Jan. 1853, p. 346.)

Composition and nutritive value of Fodder (Völeker, *Highland Agric. Soc. J.* July, 1853, p. 36.—Way, *Roy. Agr. Soc. J.* 1853, p. 561; *Jahresber.* 1853, p. 759).

Nutritive value of Rape-cake (Wolff, Pharm. Centr. 1853, p. 697).

On the Feeding of animals and especially on the effect of particular kinds of fodder on Pigs (Lawes, Roy. Agr. Soc. J. xiv. [2]).

Comparison between Sugar and Starch as ingredients of the Food of animals (Lawes and Gilbert, Chem. Gaz. 1854, p. 396; Jahresber. 1854, p. 787).

Composition and nutritive value of the Waste derived from the grinding of Peas, Barley, Rice, Oats, &c. (Anderson, Highland Agr. Soc. J. new series, xliii. 197).

Nutritive value of various kinds of Fodder, and determination of the quantities of Water and Nitrogen contained in them (Pierre, Compt. rend. xl. 658; xli. 47, 138, 566; Jahresber. 1855, p. 888).

Composition of Oil-cake from various sources (Anderson, Highland Agr. Soc. J. 1855, No. 48, p. 552; No. 49, p. 532).

Nutritive value of various waste products, especially of the Residues from the distillation of Spirit from Grain and Potatoes, and of Brewers' waste (Ritthausen, J. pr. Chem. lxvi. 289).

Ash of Barley-malt, Wine-lees, and Malt-germs (Scheven, *ibid.* 315).

Nutritive value of Elm-, Vine-, and Poplar-leaves (Pierre, Ann. Ch. Phys. [3] xlviii. 179).

Amount of nutritive matter in Mangold-wurzel and its relation to the specific gravity (Anderson, Highland Agr. Soc. J. 1856, No. 51, p. 174; Chem. Centr. 1856, p. 226).—On the constituents of Cabbage-heads at various stages of their development (Anderson, *ibid.* No. 51, p. 196; Chem. Centr. 1856, p. 232).

Reduction of the nutritive value of various kinds of Fodder to that of Hay as a standard (Korber, Chem. Centr. 1856, p. 843).

Composition of Carrots (Ritthausen, Chem. Centr. 1857, p. 14).

Composition of St. John's bread, *Artocarpus incisa* (Völcker, Zeitschr. d. deutschen Landwirthe, 1856, p. 18; Chem. Centr. 1857, p. 85).

On Buckwheat (Pierre, Compt. rend. xlvii. 710).

Composition of Cotton-seed cake (Anderson, Highland Agr. Soc. J. new series, No. 60, p. 287; Chem. Centr. 1858, p. 327).

Composition of the Husks of Rape-seed (J. Lehmann, Highland Agr. Soc. J. new series, No. 59, p. 196; Chem. Centr. 1858, p. 328).

Determination of the amount of Nitrogen, and thence of Albuminous matters, in Acorns, Horse-chestnuts, Buckwheat flour and husks (G. J. Mulder, Scheik. Onderzoek, i. No. 2, p. 73; Chem. Centr. 1858, p. 717).

Examination of Artificial Fodders (Lawes, Roy. Agr. Soc. J. xix. pt. 1).

Digestibility of Earthy Phosphates, when added in the finely pulverised state to Fodder (J. Lehmann, Ann. Ch. Pharm. cviii. 267; Rép. Chim. app. i. 253).

**FOLIATED TELLURIUM.** See NAGYAGITE.

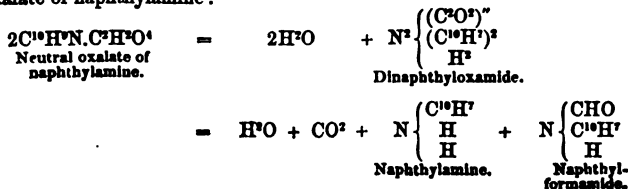
**FOOD.** See NUTRITION.

**FORMAMIDE.**  $\text{CH}^{\text{N}}\text{NO} = \text{N} \begin{Bmatrix} \text{CHO} \\ \text{H} \\ \text{H} \end{Bmatrix}$ .—Discovered in 1863 by Hofmann

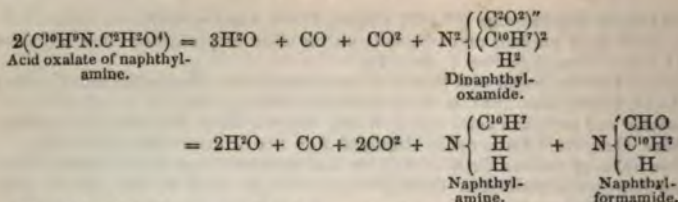
(Chem. Soc. J. xvi. 72). Prepared by heating formate of ethyl saturated with dry ammonia to 100° C. for two days in sealed tubes, then distilling, and collecting apart that which passes over at 195° C. It is a transparent colourless liquid, which does not exhibit any tendency to crystallise, even when kept for several weeks over oil of vitriol. Under the ordinary pressure, it boils between 192° and 195° C., but is resolved at the same time into carbonic oxide and ammonia:  $\text{CH}^{\text{N}}\text{NO} = \text{CO} + \text{NH}^{\text{N}}$ . In a partial vacuum, which lowers the boiling point to 140°, it may be distilled without the slightest decomposition. By the action of acids or of alkalis, it is resolved into ammonia and formic acid. By distillation with phosphoric anhydride, it is converted into hydrocyanic acid.

**Naphthylformamide.**  $\text{C}^{11}\text{H}^{\text{N}}\text{NO} = \text{N} \begin{Bmatrix} \text{CHO} \\ \text{C}^{10}\text{H}^{\text{N}} \\ \text{H} \end{Bmatrix}$ . (Zinin, Ann. Ch. Pharm. cviii.

228.)—Produced, together with dinaphthylxamide, by the action of heat on neutral or acid oxalate of naphthylamine:







The acid salt is the more advantageous of the two for the preparation of naphthylformamide, as it yields this product in larger proportion. It melts at about  $200^{\circ}\text{C}$ . giving off carbonic oxide and carbonic anhydride, together with a large quantity of water, and leaves a residue amounting to two-thirds of the salt, which solidifies in a radio-crystalline mass on cooling. Hot alcohol dissolves out the naphthylformamide, leaving the dinaphthylamide, and on cooling deposits it in long white needles. The compound is very soluble in water, turns red when exposed to damp air, melts at  $102^{\circ}\text{C}$ . and distills without decomposition. By the action of *acids* or *alkalis* at the boiling heat, it is easily resolved into naphthylamine and formic acid.

**Phenylformamide.** *Formanilide.*  $\text{C}^6\text{H}^7\text{NO} = \text{N} \left\{ \begin{array}{l} \text{CHO} \\ \text{C}^6\text{H}^5 \\ \text{H} \end{array} \right.$  (Gerhardt, J. Pharm.

[3] ix. 409; *Traité*, i. 237).—Prepared by heating oxalate of phenylamine, the decomposition being precisely analogous to that of oxalate of naphthylamine. The residue is exhausted with cold alcohol; the solution heated till the greater part of the alcohol is driven off, then boiled with water, and the solution filtered to separate a small quantity of red or brown matter. The filtrate, if further evaporated by heat, deposits the phenyl-formamide in oily drops which do not solidify; but if the heating be discontinued as soon as the oily drops begin to separate, and the solution then left to evaporate spontaneously, the amide is gradually deposited in very flattened, acuminate, rectangular prisms, usually very long and interlaced.

Phenylformamide is moderately soluble in cold, more freely in hot water, still more in alcohol; the aqueous solution is slightly bitter and neutral to test paper. In the dry state it melts at  $46^{\circ}\text{C}$ ., and may then be cooled several degrees below this temperature without solidifying, but if agitated with a glass rod, it solidifies immediately. Under water it melts more easily and remains liquid after cooling. It likewise retains its fluidity after being distilled. It begins to give off vapours, even at the heat of the water-bath. *Acids* and *alkalis* decompose it slowly in the cold, more quickly at the boiling heat, into formic acid and phenylamine. When heated with strong sulphuric acid, it gives off carbonic oxide without blackening, and is converted into phenyl-sulphuric acid.

**FORMANILIDE.** See the last article.

**FORMENAMINE.** The name given by Cloez to the first of the three bases which he obtained by the action of ammonia on dibromide of ethylene. (See ETHYLENE-BASES, ii. 585.)

**FORMENE, TRINITRATED.** Syn. with NITROFORM (*q. v.*)

**FORMIC ACID.**  $\text{CHO}^2 = \frac{\text{CHO}}{\text{H}}\text{O}$ . *Acidum formicum.* *Ameisensäure.*

(*Gm.* vii. 268; *Gerh.* i. 255; *Handw. d. Chem.* 2 Aufl. i. 668).—This acid, which is the first term of the adipic series  $\text{C}^n\text{H}^{2n}\text{O}^2$ , derives its name from the ant (*formica*), from which it was first obtained. The acid nature of these insects has long been known. Samuel Fischer first subjected them to distillation, and obtained an acid liquid; Marggraf, Arridson and Oehr, Hermbstädt, and Richter examined the acid more minutely. Fourcroy and Vauquelin pronounced it to be a mixture of acetic and malic acids, a statement which was afterwards completely refuted by Süersen and Gehlen. Berzelius, Göbel, Döbereiner, Liebig, and Pelouze examined the most important relations of formic acid. Its formation from inorganic materials was first effected by Berthelot.

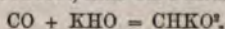
*Occurrence.*—1. In the animal kingdom. In ants, especially the red ant (*Formica rufa*), these insects projecting it from their bodies as a defence against their enemies. According to Fr. Will (*Jahresber. d. Chem.* 1847–8, p. 546), the corrosive substance in caterpillars, especially in *Bombyx processionea*, likewise consists of formic acid. It exists in the free concentrated state in all parts of the caterpillar, but especially in the faeces, in the yellowish green juice which exudes on making an incision into the insect, and lastly, in the hollow, very brittle hairs. The acid occurs also in several secretions of the human body, viz. in the blood, in the urine (Campbell, *Chem. Gaz.* 1853, p. 310), in the fluid of the spleen, in the flesh juice (Scheerer, *Ann. Ch.*

Pharm. lxi. 196), and in the perspiration (Schottin, Jahresber. d. Chem. 1852, p. 704). Small quantities of it have been found in guano (Lucius, Ann. Ch. Pharm. ciii. 105).

2. *In the vegetable kingdom*, partly perhaps as a product of decomposition. It is found in commercial oil of turpentine, whence it may be extracted by agitation with water (Wiggers, Ann. Ch. Pharm. xxxiv. 235); being doubtless formed by oxidation in the air; it imparts an acid reaction to the oil, and passes over as an aqueous acid when the oil is distilled with water (Weppen, Ann. Ch. Pharm. xli. 294). When oil of turpentine is kept in leaden vessels, crystals of formate of lead are sometimes produced (Laurent, J. pr. Chem. xxvii. 316). Fr. Müller (Arch. Pharm. [2] 149) states, though not positively, that formic acid is sometimes produced in a similar manner from oil of lemons. It occurs in the needles of *Pinus Abies*, somewhat more abundantly in those which fall off, than in those which are dried while fresh and green (Aschoff, N. Br. Arch. xl. 274), being probably formed therein by oxidation of oil of turpentine. In pine-needles, which had been used for litter, and had stood for several months made up into a heap and exposed to the air, the acid was formed so abundantly that on opening the heap a very sour smell of ants was emitted (Redtenbacher, Ann. Ch. Pharm. xlvii. 148). The juice of houseleek (*Sempervivum tectorum*), when distilled, yields an acid which reduces the noble metals like formic acid, but forms with mercurous nitrate a white precipitate, from which the metal is not reduced till the mixture is heated (Döbereiner, Schw. J. lxiii. 368). According to Gorup-Besanez (Ann. Ch. Pharm. lxi. 369), the fruit of the soap-tree (*Sapindus saponaria*) distilled with water and sulphuric acid yields a distillate containing formic and butyric acids. Tamarinds similarly treated yield formic and acetic acids, and emit an odour of butyric acid. Gorup-Besanez considers it not improbable that these acids may be formed by oxidation from the tartaric acid originally contained in the fruits. Formic acid is also found in the juice of the stinging nettle. (Gorup-Besanez, Ann. Ch. Pharm. lxii. 267.)

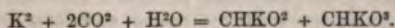
3. *In mineral waters*.—In the water of Prinzhofen, near Straubing (Pettenkofer, Kastn. Arch. vii. 104); in that of Brückenau, together with acetic, propionic, and butyric acids, the formic acid constituting 85 per cent. of the entire amount of volatile fatty acids (Scheerer, Ann. Ch. Pharm. xcix. 257), and in the deposit from the waters of Marienbad. (Lehmann.)

*Formation*.—a. *From Inorganic materials*.—1. By the action of carbonic oxide at a high temperature on moist hydrate of potassium, the bodies simply uniting and yielding formate of potassium (Berthelot, Ann. Ch. Pharm. xevii. 125):



The absorption of the gas and production of formic acid take place more quickly when a considerable quantity of water is present, than when the potash is merely moistened; alcohol and wood-spirit accelerate it still further, and ether most of all; glycerin, on account of its viscosity, has but little effect, and acetic ether none at all; in short, the effect of any liquid in accelerating the action appears to be proportional to its power of dissolving the carbonic oxide. Similar results are obtained when caustic soda, baryta, or lime is used in place of potash. (Berthelot, Ann. Ch. Phys. [3] lxi. 463.)

2. Potassium spread on the inner surface of a vessel filled with carbonic anhydride, and standing over lukewarm water, is converted in 24 hours into a mixture of formate and acid carbonate of potassium (Kolbe and R. Schmidt, Ann. Ch. Pharm. cxix. 251):



b. *From Organic materials*, chiefly by oxidation, formic acid being, with the exception of oxalic acid and carbonic anhydride, the most highly oxidised of all carbon-compounds.

1. In the oxidation of wood-spirit by the air in presence of platinum, or by nitric acid (Dumas and Peligot).—2. By heating wood-spirit with a mixture of lime and hydrate of potassium (Dumas and Stas).—3. In the decomposition of chloroform, bromoform, or iodoform, by potash.—4. In the decomposition of hydrocyanic acid by potash, or by the stronger mineral acids (Pelouze, Ann. Ch. Phys. xlviii. 395; Geiger, Ann. Ch. Pharm. i. 44).—5. In the decomposition of oxalic acid by heat (Gay-Lussac, Ann. Ch. Phys. xlvii. 218). When the oxalic acid is heated alone, the quantity of formic acid obtained is very small, but it is greatly increased by distilling the oxalic acid with glycerin or mannite (Berthelot, p. 684).—6. By the combustion of alcohol or ether in the glow lamp (A. Connell, Phil. Mag. [3] xi. 512).—7. In the preparation of iodoform from alcohol, iodine, and potassium (Bouchardat).—8. By the action of the air on an alcoholic solution of potash (A. Connell, N. Ed. Phil. J. xiv. 231).—9. By heating alcohol with nitric acid (Gaultier de Claubry, J. Pharm. xxv. 764; Dalpiaz, J. Pharm. [3] v. 239).—10. In the decomposition of



chloral or bromal by aqueous potash (Liebig).—11. By boiling chloracetic acid with excess of potash (Dumas).—12. By heating gelatin with aqueous chromic acid (Schlieper, *Ann. Ch. Pharm.* lix. 1).—13. By exposing oil of turpentine to the air, or heating it with aqueous chromic acid (Weppen, *Ann. Ch. Pharm.* xli. 294).—14. By distilling aqueous tartaric acid with peroxide of manganese (Döbereiner, *Gilb. Ann.* lxxi. 107).—15. By distilling the following substances with peroxide of manganese and dilute sulphuric acid: tartaric acid or cane-sugar (Döbereiner, *Ann. Ch. Pharm.* iii. 144); starch (Wohler, *Pogg. Ann.* xv. 307); mucic acid, milk-sugar, starch, woody fibre, marsh-mallow root, fibrin (C. G. Gmelin, *ibid.* xvi. 55); alcohol (C. G. Gmelin; Connell, *N. Ed. Phil. J.* xiv. 240; L. Gmelin, *Pogg. Ann.* xxviii. 508); suberic acid (Brandes, *N. Br. Arch.* xxi. 319); glucose, which likewise yields formic acid when treated with sulphuric acid and chromic acid or ferric oxide (Hünefeld, *J. pr. Chem.* vii. 44);—albumin, fibrin, casein, and gelatin, which likewise yield formic acid with acid chromate of potassium and sulphuric acid; in both cases the formic acid is accompanied by other acids of the series  $C^mH^{m+2}O^2$ , and a variety of other products (Guckelberger, *Ann. Ch. Pharm.* lxiv. 39; Jahresber. 1847–8, pp. 847–854). When some of these compounds—starch, for example—are thus treated, there is given off, together with the formic acid, a strong smelling volatile oil (furfural), which, if the distillate be saturated with a fixed alkali, imparts a yellow colour to the liquid, but passes off, or is decomposed when the solution is evaporated. In this impure distillate, and in another obtained from starch, oxide of manganese, and hydrochloric acid, Tinnermann (*Pogg. Ann.* xv. 307) thought that he had discovered two peculiar acids, to which he gave the names of *pyrogenic* and *amylenic* acids. When alcohol is treated with sulphuric acid and oxide of manganese, no oil like furfural passes over, but a large quantity of acetic acid.—16. Sugar, starch, gum, woody fibre, cereal grains, and other organic substances, yield much more formic acid when distilled with strong sulphuric acid, or a mixture of that substance with an equal bulk of water, than when treated with sulphuric acid and peroxide of manganese: for the latter converts a considerable quantity of the formic acid into carbonic acid and water. Before carbonisation, a volatile oil passes over; but as soon as carbonisation takes place, the distillate consists of colourless formic acid. Phosphoric acid, stannic chloride, and other dehydrating substances, act like sulphuric acid (Emmet, *Sill. Am. J.* xxxii. 140; also *J. pr. Chem.* xii. 120). These statements have been verified by Erdmann (*J. pr. Chem.* xii. 124) and Stenhouse (*Phil. Mag.* [3] xviii. 122; also *Ann. Ch. Pharm.* xxxv. 301).—17. A solution of tartaric acid containing a little sulphuric acid heated with permanganate of potassium yields formic and carbonic acids,  $C^mH^mO^4 + O^2 = 2C^mH^mO^2 + 2CO^2 + H^2O$ ; but if the solution is neutralised by an alkali, the whole of the formic acid is oxidised to carbonic acid (Péan de St. Gilles, *Ann. Ch. Phys.* [3] iv. 374).—18. When linseed-oil is heated with sulphuric acid, a large quantity of formic acid passes over, together with sulphurous acid (Sacc, *Ann. Ch. Pharm.* li. 214).—19. Sugar, starch, cotton, &c., treated with chloride of lime containing free lime, yield formate of calcium; if no free lime be present, carbonic acid is produced instead of formic acid: on a solution of sugar the action is very violent. Chloride of lime containing free lime forms, with a solution of gelatin, formate of calcium and ammonia (Bastick, *Pharm. J. Trans.* vii. 467; Jahresber. d. Chem. 1847–8, 381).—20. By treating crude oil of asafetida with caustic soda, acetic acid being likewise formed, and sulphuretted hydrogen given off. The gummy portion of asafetida, when subjected to dry distillation, yields formic acid, with a small quantity of acetic acid.—21. Oil of mustard and oil of garlic treated with nitric acid yield formic acid, together with oxalic (Hlasiwetz, *J. pr. Chem.* li. 355).—22. An aqueous solution of acetone containing sulphuric acid yields, by electrolysis, acetic and formic acids, together with oxygen, hydrogen, and carbonic anhydride. The formic acid is, perhaps, produced by the oxidation of the methyl contained in the acetone (i. 26). (Friedel, *Ann. Ch. Pharm.* cxii. 376.)

Formic acid has been found among the products of the destructive distillation of peat. (Sullivan, *Atlantis*, i. 185; Jahresber. d. Chem. 1858, p. 280.)

By distilling aloes with very dilute sulphuric acid, Ed. Simon (*N. Br. Arch.* xxix. 186) obtained a distillate which reduced silver-salts like formic acid; but yielded crystals with oxide of lead different from those of formate of lead. In the weathering of brown coal containing iron pyrites, a strong odour of formic acid is often evolved (Anthon, *Repert.* lxxxviii. 106). When 4 at. of iron-flings are distilled with  $1\frac{1}{2}$  at. tartaric acid ( $C^4H^4O^6$ ), the water in the receiver acquires an odour of ants, and the property of reducing metallic oxides (Artus, *J. pr. Chem.* xii. 251). According to Göbel (*N. Tr. x.* 1, 34), formic acid is produced in the dry distillation of argol. This, however, has not been satisfactorily proved.

Klinger (*Ann. Ch. Pharm.* cvi. 13) found small quantities of formic and propionic acids, together with large quantities of acetic and butyric acids, in the products of the fermentation of diabetic urine; other observers, however, have found only acetic and butyric acids. (Jahresber. 1858, p. 571.)



According to Geuther (Ann. Ch. Pharm. cix. 73) and Lieben (*ibid.* cxii. 326), formic acid is produced by the action of carbonic oxide on ethylate of sodium. Lieben, however, and Wanklyn (Phil. Mag. [4] xviii. 391) attribute this result to the presence of hydrate of sodium in the ethylate (p. 682).

*Preparation.*—*a. Of the aqueous acid.*—1. *From Ants.*—Red ants previously mashed, or their expressed juices, are distilled; the distillate is saturated with potash, soda, oxide of lead, or oxide of copper; the solution evaporated, whereupon the volatile oil of ants passes off together with the water; and the residue, or the formate purified by recrystallisation, is distilled with dilute sulphuric acid.

The very dilute acid thus obtained is saturated with carbonate of potassium (Richter, Süersen), sodium (Lowitz, Gehlen), or copper (Gehlen); and the dried residue, or, when oxide of copper is used, the crystals purified by repeated crystallisation are distilled with oil of vitriol (Richter, Gehlen), or with a mixture of 1 pt. oil of vitriol and  $\frac{1}{2}$  water (Süersen), or with pulverised acid sulphate of potassium (Lowitz). If the quantity of water present is too small, a large proportion of the formic acid is decomposed; hence strong sulphuric acid cannot be used for the distillation. Any sulphurous acid that may be present is removed by continued digestion with red lead; also hydrochloric acid (proceeding from the carbonate of potassium) by red lead, or better by oxide of silver. (Göbel.)

The residue left in the preparation of *oil of ants* (a pharmaceutical product obtained by distilling 2 pts. of red ants with 4 pts. rectified spirit of 60 per cent., and an equal quantity of water) contains a considerable quantity of formic acid, and may be used for its preparation. The residue is pressed; the expressed liquid left to itself for a while; the fatty oil which collects on the surface removed; the subjacent liquid neutralised with an alkali, filtered and evaporated; and the residual salt mixed with half its weight of strong sulphuric acid diluted with an equal quantity of water, and distilled till the liquid begins to pass over turbid. This first distillate consists of tolerably pure formic acid. The turbid liquid which follows still contains formic acid; it may be neutralised with carbonate of barium, and used for the preparation of pure barytic formate. (Handw. 2<sup>te</sup> Aufl. i. 688.)

2. *From Tartaric acid.*—10 pts. of tartaric acid are mixed with 14 pts. of oxide of manganese and from 30 to 45 pts. of water, and distilled in a capacious retort. (Döbereiner.)

3. *From Sugar or Starch with Peroxide of Manganese and Sulphuric acid.*—*a. A* solution of 1 pt. sugar in 2 pts. water is heated to 60° C., with 2½ or 3 pts. of finely pounded manganese in a copper still, which, as the liquid is very apt to froth up, must have at least 15 times the bulk of the mixture; a third part of a mixture of 3 pts. oil of vitriol and 3 pts. water is then gradually added, whereupon carbonic acid gas loaded with vapour of formic acid immediately escapes with violence. The head and condensing tube must now be quickly put on, and when the violent action has subsided, the other two-thirds of the dilute sulphuric acid added, the mixture being stirred all the while; after which the liquid is gradually distilled almost to dryness. The distillate, which is transparent and colourless, and still contains volatile oil (furfural), is saturated with chalk (the distillate from 100 pts. of sugar saturates from 31 to 38 pts. of chalk); and the filtrate evaporated to the crystallising point; or, if it be desired to obtain the acid, the distillate is saturated with carbonate of sodium, evaporated, and 7 pts. of the dry residue distilled with a mixture of 70 pts. oil of vitriol and 4 pts. water (Döbereiner, Ann. Ch. Pharm. iii. 144). This process is a very good one; but the formic acid which it yields is slightly contaminated with acetic acid. To remove this impurity, the distillate should be saturated, while yet warm, not with carbonate of sodium, but with carbonate of lead, and the solution evaporated to the crystallising point; the more soluble acetate of lead remains principally in the mother-liquor; and the formate of lead thus obtained must be distilled with a mixture of equal parts of oil of vitriol and water.

*B.* 1 pt. of starch is mixed with 4 pts. of finely pounded manganese and 4 pts. of water in a copper still; 4 pts. of oil of vitriol added by small portions, and with constant stirring; the vessel heated by a slow fire till the contents begin to froth up; the head and condensing tube then put on, and the distillation continued till 4½ pts. of the liquid have passed over. This liquid has a density of 1.025 at 10° C., and saturates 10.6 per cent. of dry carbonate of sodium. If the distillation is performed in a retort instead of a still, it is necessary, in order to prevent frothing over, to take only 3.7 pts. of manganese, 3 water, and 3 oil of vitriol to 1 pt. of starch; the retort must have 10 times the bulk of the mixture. The product thus obtained amounts to 3.35 pts. of a distillate of specific gravity 1.042, which neutralises 15 per cent. of dry carbonate of sodium. The distillate obtained either from the retort or from the still is clouded by a white substance; and if the distillation has been carried too far, the liquid also contains sulphurous acid. It must therefore be neutralised with carbonate of calcium; milk of lime added in excess to convert the soluble acid sulphite of calcium into



the neutral insoluble sulphite; the filtrate evaporated to dryness; and 10 pts. of the resulting formate of calcium distilled, either with 8 pts. oil of vitriol and 4 water, whereby 9 pts. of formic acid are obtained, having a density of 1.075, or with 8 pts. oil of vitriol and  $1\frac{1}{2}$  water, by which a highly concentrated acid is obtained. The strongest acid that can be prepared in this manner is obtained by distilling 18 pts. of finely pounded formate of lead with 6 pts. oil of vitriol and 1 pt. water in a chloride of calcium bath. The distillate has a density of 1.110 at  $10^{\circ}$  (Liebig). Cloez ([3] J. Pharm. iv. 306) mixes 500 grm. of starch with 2000 grm. of manganese; places the mixture in a still having a capacity of 25 or 30 litres; adds 1 litre of water, then a mixture of 2 kilogrammes of oil of vitriol with 2 litres of water, stirring the mixture well; and distils, adding hot water in proportion as the liquid passes over: from 12 to 15 litres of a strongly acid liquid may be thus obtained over, containing about 412 grammes of formic acid ( $\text{CH}_2\text{O}^2$ ).

4. *From Sugar, Starch, or Woody fibre, with Sulphuric acid.*—One measure of oil of vitriol, 1 measure of water, and 1 measure of rye, wheat, oats, or coarsely bruised maize, are heated together in a glass retort till the liquid boils; one measure of water is added as soon as the mass becomes thoroughly black; the liquid distilled till one measure of distillate has passed over; another measure of water added to the residue; and the distillation repeated with a fresh receiver. The first distillate consists of strong formic acid, generally free from sulphurous acid; the second is very dilute and often contains sulphurous acid; this impurity may be removed by agitating the cold liquid for a short time with peroxide of lead. The organic matter used in this process, being of a granular nature, does not swell up so much: hence the vessels used need not be so large as those required in the preceding processes (Emmet, Sill. Am. J. xxxii. 143). Carbonisation takes place before boiling, so that there is no occasion to wait till the liquid boils. The addition of water causes the hot mass to froth over: hence it is necessary to let the mixture cool before adding fresh water. In all cases frothing and boiling over are very likely to be produced by a slight rise of temperature: hence the retort should hold at least five times as much as the volume of the mixture. The distillate is free from acetic acid, but contains furfural, which may be removed by ether (Erdmann, J. pr. Chem. xii. 124). Stenhouse (Phil. Mag. [3] xviii. 122) proceeds in the same manner as Emmet for the preparation of furfural and formic acid, excepting that he uses wheat-flour, saw-dust, or chaff, instead of grain.

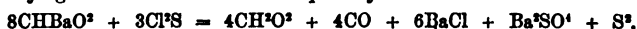
5. *From Oxalic acid.*—An intimate mixture of oxalic acid and very fine sand is distilled in a glass retort, and the distillate freed from oxalic acid by frequent rectification. This process yields very pure formic acid in a highly concentrated state. (Gerhardt, Ann. Ch. Phys. [3] vii. 130.)

A much larger product may be obtained by distilling the oxalic acid with glycerin. Oxalic acid,  $\text{C}^2\text{H}^2\text{O}^4$  contains the elements of carbonic anhydride,  $\text{CO}^2$ , and formic acid,  $\text{CH}_2\text{O}^2$ , and is actually resolved into these compounds by heat; but when it is heated alone, or even with sand, the temperature rises so high that the greater part of the formic acid is further resolved into carbonic oxide,  $\text{CO}$ , and water  $\text{H}^2\text{O}$ ; but the addition of glycerin, which takes no part in the decomposition, enables it to take place at a lower temperature, and the whole of the formic acid is then obtained. When equal weights of commercial oxalic acid and syrupy glycerin (a kilogramme of each) and from 100 to 200 grammes of water, are gently heated (scarcely above  $100^{\circ}\text{C}$ .) in a capacious retort, a brisk evolution of carbonic anhydride soon begins, and after 12 to 15 hours, the whole of the oxalic acid is decomposed without any evolution of carbonic oxide. A small quantity of the resulting formic acid distils over with the water; but the larger portion remains in the retort together with the glycerin, and may be separated by distilling the residue with half a litre of water, renewing the water as it distils, till 6 or 7 litres of liquid have passed over. The glycerin which remains may be used for the conversion of fresh quantities of oxalic acid. The decomposition must be conducted slowly, as, if too much heat is applied, the temperature rises to between  $190^{\circ}$  and  $200^{\circ}$ , and carbonic oxide is evolved. (Berthelot, Ann. Ch. Phys. [3] xlv. 477.) This is the best of all methods of preparing formic acid.

b. *Preparation of the pure concentrated acid,  $\text{CH}_2\text{O}^2$ .*—1. Pulverised formate of lead dried by heat is introduced into a long glass tube, from 4 to 6 lines in width, one end of which is drawn out into a narrow neck, turned downwards and inserted into a small receiver; sulphuretted hydrogen dried by chloride of calcium is passed into the tube at the other end, till the lead-salt is completely decomposed; a gentle heat applied to drive the formic acid into the receiver; and the acid repeatedly boiled to free it from sulphuretted hydrogen. If the tube be too strongly heated, the acid becomes contaminated with decomposition-products containing sulphur (Liebig).—Bineau (Compt. rend. xix. 769) passes dry carbonic anhydride through the distillate to drive off the sulphuretted hydrogen, and rectifies it, rejecting the first portion, which still smells of sulphuretted hydrogen.

2. By mixing 8 at. of a dry formate, the barium-salt for example, with 8 at. water,

gradually adding 3 at. chloride of sulphur,  $\text{Cl}_2\text{S}$ , distilling between  $110^\circ$  and  $122^\circ\text{C}$ ., and rectifying the distillate over a small quantity of formate of lead:



(Heintz, Pogg. Ann. xviii. 458.)

*Properties.*—The most concentrated acid solidifies at  $-1^\circ\text{C}$ . in shining laminae, which melt at  $+1^\circ$ . At ordinary temperatures it forms a thin, transparent, and colourless liquid, of specific gravity 1.2353, which boils at  $98.5^\circ$  (bar.  $27''\ 10''$ ) (Liebig).—According to Kopp (Jahresber. 1847–8, p. 68), the specific gravity is 1.2227 at  $0^\circ$ , and the boiling point  $105.3$  (bar. 760 mm.); according to Person (Jahresber. 1847–8, p. 91), the acid boils at  $100^\circ$ ; according to Roscoe (Chem. Soc. J. xv. 271), at  $101.1^\circ$  under a pressure of 758 mm. of mercury. The vapour-density, between the temperatures  $111^\circ$  and  $118^\circ$ , varies from 2.125 to 2.14 (Bineau, Compt. rend. xix. 769; also Pogg. lxxv. 424; Compt. rend. xxiii. 416). The strongest acid fumes slightly in the air, has a pungent sour taste, and is so corrosive that a single drop placed upon a soft part of the skin produces intolerable pain, causing the part to swell and turn white, afterwards drawing the skin together and producing a painful ulcer (Liebig). The dilute acid has a peculiar pungent and sour smell, and a purely acid taste.

Formic acid mixes with water in all proportions, with diminution of specific gravity and without rise of temperature. According to Liebig, an aqueous acid containing 1 at. water ( $\text{CH}^2\text{O}^2.\text{H}^2\text{O}$ ), and boiling at the fixed temperature of  $106^\circ\text{C}$ ., is obtained by distilling 18 pts. formate of lead with 6 pts. oil of vitriol and 1 pt. water. According to Roscoe (Chem. Soc. J. xv. 271), formic acid (like all other acids) possesses no hydrate of constant boiling point at all pressures; but any number of mixtures of formic acid and water can be made, each of which, when distilled under a given pressure, will undergo no change in composition, and therefore will boil at a fixed point, but will undergo decomposition when boiled under any other pressure. Under the ordinary atmospheric pressure (760 mm.), a liquid containing 77.6 pts. acid to 22.5 pts. water undergoes no change by distillation, boiling at the temperature of  $107.1^\circ\text{C}$ .; and all mixtures containing more acid or more water than this quantity, when distilled under the above conditions, ultimately attain this same fixed boiling point and constant composition. When distilled under a higher pressure, however, this aqueous acid undergoes a change of composition. Under a pressure of 1.83 met. of mercury, the residual liquid attains a composition of 83.2 per cent. real acid and boils unchanged at  $134.6^\circ\text{C}$ . Under a pressure of 1.35 met. of mercury, the aqueous acid boils constantly at  $124.1^\circ\text{C}$ ., and attains the strength corresponding to 80 per cent. of real acid.

Formic acid dissolves in all proportions in alcohol, being partly converted into formate of ethyl.

*Decompositions.*—1. The vapour of the boiling concentrated acid may be set on fire in the air, and burns with a dull blue flame (Liebig). Platinum-black, repeatedly moistened in the air with aqueous formic acid, causes slow combustion of the acid, accompanied by evolution of heat and a hissing noise, the products of the combustion being carbonic acid and water. If the platinum-black has been previously charged with oxygen by exposure to the air, it will oxidise small quantities of the acid, even out of contact of air. Spongy platinum, slightly moistened in the air with formic acid containing not more than  $1\frac{1}{2}$  at. water, becomes almost instantly red-hot, producing water and carbonic acid (Döbereiner). 2. Chlorine decomposes the acid and its salts completely, converting them after a while into carbonic and hydrochloric acids. (Cloeze, Ann. Ch. Phys. [3] xvii. 297):



3. Nitric acid decomposes formic acid. (Arvidson.)

4. Aqueous iodic or periodic acid acts violently on formic acid at a boiling heat, evolving carbonic anhydride and iodine (Benckiser, Ann. Ch. Pharm. xvii. 258). At a temperature near  $100^\circ\text{C}$ . aqueous iodic acid completely converts formic acid, in the course of twenty minutes, into water and carbonic anhydride; but a trace of hydrocyanic acid prevents the decomposition, even at a boiling heat. (Millon, Compt. rend. xix. 271.)

5. Strong sulphuric acid, at a gentle heat, decomposes formic acid and its salts, converting them into water and carbonic oxide, with strong effervescence, but without blackening:  $\text{CH}^2\text{O}^2 = \text{H}^2\text{O} + \text{CO}$ . (Döbereiner.)

6. Formic acid reduces the oxides of the noble metals, yielding water and carbonic anhydride. It reduces mercuric oxide with effervescence when heated. From mercurous or mercuric nitrate, it throws down metallic mercury at a boiling heat; boiled with a solution of mercuric chloride, it throws down calomel (Göbel, Döbereiner). A hot aqueous solution of mercuric chloride mixed with formate of

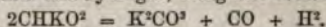


potassium or sodium, and kept for two or three hours at a temperature between 70° and 80° C., deposits all the mercury in the form of calomel; but if kept constantly at a boiling heat, it yields the mercury in the metallic state (Bonsdorff, Pogg. Ann. xxxiii. 73). This reducing action is, however, prevented by the presence of chloride of potassium, sodium, or ammonium, and even by adding acetic acid to the solution of mercuric chloride (H. Rose, Pogg. Ann. cvi. 500). Silver-oxide and those of its salts which are soluble in water are reduced by formic acid with the aid of heat; the salts are more quickly reduced by formate of sodium (Göbel, Döbereiner). Solutions of gold, platinum, and palladium are not reduced by continued boiling with free formic acid, because the acid gradually volatilises; but they are completely reduced by formate of sodium, which in some cases throws down spangles, in others, as with platinum, precipitates a black possessing great power of inducing combustion (Göbel). The aqueous acid converts platinous oxide and platinate of sodium into platinum-black, with brisk evolution of carbonic acid (Döbereiner, Pogg. xxviii. 180; Schw. lvi. 289). At a boiling heat, it reduces protochloride of platinum to the metallic state. (Berzelius, Pogg. xxxvi. 8.)

7. Peroxides with dilute sulphuric acid convert formic acid into carbonic anhydride and water. (Liebig.)

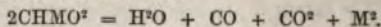
8. Formate of potassium, moderately heated with excess of hydrate of potassium, gives off hydrogen, and is converted into oxalate,  $2\text{CHKO}^2 = \text{C}^2\text{K}^2\text{O}^4 + \text{H}^2$ . (Peligo, Ann. Ch. Phys. lxxiii. 220; Dumas and Stas, *ibid.* lxxiii. 123.)

**Formates.**—The affinity of formic acid for bases is, according to Arvidson, greater than that of acetic acid. It is monobasic, the general formula of its salts being  $\text{CHMO}^2$ . There are, however, a few double and acid formates produced by the union of two metallic formates or of a metallic formate with formic acid, analogous in fact to the double chlorides, acid acetate of potassium, &c., not to the double salts of dibasic acids. They are obtained by dissolving the bases or their carbonates in the aqueous acid, and evaporating. The formates of the fixed alkali-metals ignited out of contact of air, leave alkaline carbonates slightly blackened by charcoal, a combustible gas, probably carbonic oxide and hydrogen, being also evolved:

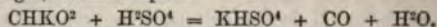


Formate of barium yields the products just mentioned, together with gaseous hydrocarbons, viz. marsh-gas, ethylene, and tritylene. (Berthelot, Ann. Ch. Phys. [3] liii. 69; Jahresber. d. Chem. 1858, p. 216.)

The formates of uranium, bismuth, zinc, cadmium, lead, cobalt, nickel, and copper, when heated to redness, leave a regulus of metal, which at a stronger heat assumes the metallic lustre (Göbel). In these decompositions, water, carbonic anhydride, and carbonic oxide are doubtless evolved:



Sulphuric acid heated with the formates decomposes them, forming a sulphate, water, and carbonic oxide gas, which escapes:

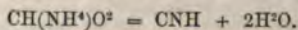


Platinum-black, moistened with the solution of an alkaline formate, converts it into carbonate (Döbereiner, Ann. Ch. Pharm. xiv. 14). The aqueous solutions of formates, heated with solutions of the noble metals, *e.g.* mercury and silver, in acids, reduce the metals, with evolution of carbonic anhydride.

All formates are soluble in water: their aqueous solutions form dark red mixtures with ferric salts.

*Formate of Aluminium* may be obtained by precipitating formate of barium with sulphate of aluminium in equivalent proportion, and evaporating the filtrate. It crystallises with difficulty (Liebig). It tastes sweet and rough; reddens litmus slightly; becomes moist in the air; forms a clear solution in cold water; dissolves likewise in hot water, but with instant precipitation of all the alumina (Göbel). The solution of the pure salt does not become turbid when heated; but if sulphate of potassium is present, it forms a precipitate which redissolves as the liquid cools. (Liebig.)

*Formate of Ammonium*,  $\text{CH}(\text{NH}^4)\text{O}^2$ , forms monoclinic crystals, exhibiting the combination  $\infty\text{P}\infty$ ,  $\text{oP}$ ,  $+\text{P}\infty$ ,  $+\text{P}$ ,  $[\text{P}\infty]$ . Ratio of axes,  $a:b:c = 0.884:1:1.269$ . Angle of inclined axes =  $87^\circ 28'$ ;  $\infty\text{P}\infty : +\text{P}\infty = 140^\circ 38'$ ;  $\text{oP} : [\text{P}\infty] = 124^\circ 54'$ . Cleavage parallel to  $\text{oP}$  (Grailich and Lang, Wien. Akad. Ber. xxvii. 178). It has a fresh pungent flavour, and is not poisonous (Pelouze). When suddenly heated in a retort, it is resolved into water and hydrocyanic acid (Döbereiner, Repert. xv. 425):



When gradually heated it fuses at  $120^\circ \text{C}$ . without giving off water, but evolves a

small quantity of ammonia at 140° and at 180°. It is for the most part resolved into hydrocyanic acid and water, a small portion only volatilising undecomposed (Pelouze, *Ann. Ch. Phys.* xliii. 399; also *Ann. Pharm.* ii. 57). To make the decomposition complete, the salt must be heated at the closed end of a bent tube, and the vapour passed over a part of the tube kept at a stronger heat (Liebig). The aqueous solution exposed to light in a stoppered bottle for half a year deposits a large quantity of flake and becomes alkaline (Horst, *Be. Arch.* iv. 357). The salt dissolves readily in water.

*Formate of Amyl.* See FORMIC ETHERS.

*Formate of Barium*,  $\text{CHBaO}^2$ .—Crystallises in shining transparent rhombic prisms;  $a : b : c = 0.7554 : 1 : 0.6842$ . Inclination of  $\alpha P : \alpha P$ , in the macrodiagonal principal section =  $75^\circ 35'$ ; of  $P\alpha : P\alpha$  in the basal principal section =  $97^\circ 30'$ . Ordinary combination  $\alpha P . P\alpha$  (*Fig. 494*; *Kopp's Krystallographie*, p. 265); also with the faces  $P\alpha$ ,  $2P\alpha$ , and  $\alpha P\alpha$ , more rarely  $\alpha P\alpha$  (Heusser, *Pogg. Ann.* lxxxiii. 37). The crystals are permanent in the air, have a bitter taste, dissolve in 4 pts. of cold water, but are insoluble in alcohol and in ether. The salt decomposes when heated, emitting the odour of burnt sugar.

*Formate of Bismuth*.—Soluble in water; crystallises on evaporation.

*Formate of Butyl.*—See FORMIC ETHERS.

*Formate of Cadmium*,  $\text{CHCdO}^2 + \text{H}^2\text{O}$ .—Crystallises in cubes and rhombic dodecahedrons (Göbel); in monoclinic prisms isomorphous with the zinc-salt (Heusser).  $a : b : c = 0.7546 : 1 : 0.924$ . Angle of inclined axes =  $82^\circ 55'$ ;  $\alpha P : \alpha P$  in the orthodiagonal principal section =  $105^\circ 30'$ ;  $\alpha P : \alpha P = 85^\circ 43'$ ;  $+2P\alpha$  : the principal axis =  $29^\circ 55'$ . The crystals have the faces  $\alpha P$  and  $\alpha P$  predominant, or they form short prisms with the faces  $+P$ ,  $+2P\alpha$ ,  $-P$ , and  $\alpha P\alpha$ ; or they are tabular from predominance of  $\alpha P$ , with  $-P$  and  $+2P\alpha$ , which latter often predominates to the obliteration of  $\alpha P\alpha$  (*Kopp's Krystallographie*, p. 310). The salt has a sweetish, but somewhat metallic taste, and dissolves easily in water. The crystals when heated give off their water with difficulty, and undergo sudden decomposition at a higher temperature.

*Formate of Cadmium and Barium*,  $\text{CBaCdO}^2$ .—Crystallises in rhombic prisms, whose predominant faces are  $\alpha P$ ,  $\alpha P\alpha$ , and  $P\alpha$ . Inclination of  $\alpha P : \alpha P$  in the macrodiagonal principal section =  $84^\circ 10'$ ;  $P\alpha : P\alpha$  over the principal axis =  $118^\circ 50'$ . (Handl, *Wien. Akad. Ber.* xxxii. 252).

*Formate of Calcium*,  $\text{CHCaO}^2$ .—Obtained by spontaneous evaporation in rhombic crystals, exhibiting the faces  $P$ ,  $\alpha P$ ,  $\alpha P\alpha$ ,  $\alpha P\alpha$ ,  $2P$ . Ratio of axes  $a : b : c = 0.75988 : 1 : 0.46713$ .  $P : P$  in the terminal edges =  $136^\circ 36'$  and  $121^\circ 46'$ ;  $\alpha P : \alpha P$  in the brachydiagonal principal section =  $67^\circ$  (Heusser, *Pogg. Ann.* lxxxiii. 37). Usually, however, it separates in crystalline crusts made up of small shining six-sided crystals. It has a sharp saline taste, dissolves in 8 to 10 pts. of cold water, scarcely more in warm water, insoluble in alcohol.

Göbel obtained a salt containing crystallisation-water, which crystallised in octahedrons and dodecahedrons, but gave up its water with efflorescence, even at common temperatures.

*Formate of Cerium*,  $\text{CHCeO}^2$ .—Formed by precipitating a hot concentrated solution of cerous chloride with formate of sodium, and separates on cooling as a faintly rose-coloured granulo-crystalline powder. It is very sparingly soluble. It contains water of crystallisation, which, however, it gives off completely at  $120^\circ \text{C}$ . (Liebig). According to Beringer, it still retains  $\frac{1}{4}$  at water at  $260^\circ$ . At  $200^\circ$  it intumesces without melting, gives off carbonic anhydride and hydrocarbons, and is converted, without blackening, into cerous carbonate, which when more strongly heated leaves ceroso-ceric oxide. (Liebig.)

*Chromic Formate* is a green soluble salt.

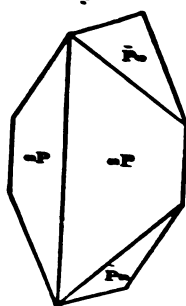
*Formate of Cobalt* forms rose-red indistinct crystals, sparingly soluble in water, insoluble in alcohol; when heated, they give off water and turn blue.

*Formate of Copper*,  $\text{CHCuO}^2 + 2\text{H}^2\text{O}$ .—Crystallises in monoclinic prisms or tables.  $a : b : c = 0.983 : 1 : 0.766$ . Angle of inclined axes =  $79^\circ 20'$ . Inclination of  $\alpha P : \alpha P$  in the clinodiagonal principal section =  $90^\circ$ ; of  $+P : +P$  in the same =  $112^\circ 18'$ ; of  $\alpha P : \alpha P = 82^\circ 30'$ . Ordinary combination  $\alpha P . \alpha P . +P$  (*Fig. 495*;

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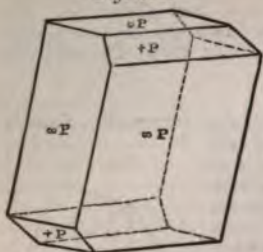
Fig. 494.





Kopp's *Krystallographie*, p. 310). According to Heusser, whose measurements agree very nearly with those of Kopp, the crystals likewise exhibit the faces  $\infty P$  and  $[\infty P\infty]$ , and often form twins, with the face of combination parallel to  $\infty P$ . Cleavage parallel to  $\infty P$ . The crystals are transparent and of a pale blue or greenish yellow colour. Specific gravity 1.81. Soluble with blue colour in 7 or 8 pts. water, and in 400 pts. alcohol of 80 per cent. They effloresce in warm air, and when heated give off inflammable products which burn with a green flame. The salt when subjected to dry distillation, leaves metallic copper, and gives off a mixture of carbonic oxide, carbonic anhydride, and hydrogen gases.

Fig. 495.



*Formate of Copper and Hydrogen; Acid Formate of Copper*,  $\text{CHCuO}^2.\text{CH}^2\text{O}^2 + \frac{1}{2}\text{H}^2\text{O}$ .—Separates, together with formate of copper and strontium, from a strongly acid solution of 2 at. formate of strontium and 1 at.

formate of copper, in monoclinic crystals, which, according to Zepharovich, exhibit the combination  $\infty P. + 2P\infty. \infty P. \infty P\infty. -P. + P$ . Ratio of axes  $a : b : c = 1 : 1.3238 : 1.1765$ . Angle of inclined axes  $= 82^\circ 31'$ . Inclination of  $\infty P : \infty P\infty = 127^\circ 15'$ ;  $+P : +P = 94^\circ 18'$ ;  $-P : -P = 100^\circ 44'$ , both in the clinodiagonal terminal edge;  $\infty P : + 2P\infty = 114^\circ 21'$ . Cleavage parallel to  $\infty P\infty$ . (K. v. Hauser, Wien. Akad. Ber. xliii. [2] 548.)

*Formates of Copper and Barium*.—Heusser obtained two of these salts from mixed solutions of the simple salts, viz. bluish green crystals having the composition  $\text{CH}(\text{Ba}; \text{Cu})\text{O}^2 + 2\text{H}^2\text{O}$ ; that is to say, formate of copper in which part of the copper is isomorphously replaced by barium; and light blue crystals, whose composition he represents by the formula  $\text{CHCuO}^2.2\text{H}^2\text{O} + 2\text{CHBaO}^2$ . Both are isomorphous with neutral formate of copper.

*Formate of Copper and Strontium*,  $(\text{CHCuO}^2.2\text{H}^2\text{O}) + 2(\text{CHSrO}^2.\text{H}^2\text{O})$ .—Obtained like the cupro-barytic salt. According to Heusser, it is likewise isomorphous with neutral formate of copper; but according to Zepharovich (Wien. Akad. Ber. xliii. [2] 545), it does not even crystallise in the same system, the crystals being not mono- but tri-clinic, and exhibiting the combination  $\infty P. \infty P\infty. \infty P\infty. \infty P'. \infty P. P\infty. \frac{1}{2}P'\infty. P'\infty. P\infty. P. \frac{1}{2}P$ . Ratio of brachydiagonal  $a$ , macrodiagonal  $b$ , and principal axis  $c = 0.7436 : 1 : 1.0103$ . Angle  $b : c$  in the left upper octant  $= 104^\circ 43'$ ;  $a : c = 95^\circ 52'$ ;  $a : b = 88^\circ 18'$ . Inclination of  $\infty P : \infty P\infty = 104^\circ 38'$ ;  $\infty P : \infty P\infty = 95^\circ 37'$ ;  $\infty P\infty : \infty P\infty = 89^\circ 47'$ ;  $\infty P\infty : \infty P = 142^\circ 31'$ ;  $\infty P\infty : P\infty = 127^\circ 59'$ . Cleavage perfect parallel to  $\infty P\infty$ ; less perfect parallel to  $\infty P\infty$ .

*Formate of Ethyl*.—See FORMIC ETHERS.

*Formates of Iron*.—The ferrous salt is obtained by dissolving ferrous hydrate in formic acid, or more easily by decomposing the barium-salt with ferrous sulphate. The colourless solution when evaporated in an open vessel deposits a basic ferric salt.

*Neutral ferric formate*,  $\text{C}^3\text{H}^3(\text{Fe}^3)\text{O}^6$  or  $\text{CH}_3\text{FeO}^3$ , is obtained by digesting moist ferric hydrate for several days in aqueous formic acid, evaporating the red-brown acid solution at about  $70^\circ \text{C}$ , and drying the residue at  $40^\circ$ . It is a light, loosely coherent powder, of the colour of levigated litharge, easily soluble in water, having an astringent taste, and acid reaction; it does not reduce nitrate of silver even at the boiling heat. (Ludwig, Arch. Pharm. [2] cvii. 1.)

Döbereiner obtained a basic ferric formate, probably  $3\text{Fe}^4\text{O}^3.\text{C}^3\text{H}^3(\text{Fe}^3)\text{O}^6$ , by boiling the solution of a ferrous salt with formate of sodium.

*Formate of Lead*,  $\text{CHPbO}^2$ , forms anhydrous shining rhombic crystals isomorphous with the barium-salt (Heusser), having a sweet, metallic, astringent taste, like that of the acetate, soluble in 36 to 40 pts. of water, but insoluble in alcohol; this last character affords a means of separating formate of lead from the acetate. Specific gravity 4.56 (Böttger and Giesecke, Jahresber. d. Chem. 1860, p. 17). It decomposes when heated, giving off a watery liquid having a disagreeable odour, but no acid reaction. Göbel obtained a formate of lead containing  $\frac{1}{2}$  at. water ( $2\text{CHPbO}^2 + \text{H}^2\text{O}$ ), which it gave off at  $100^\circ \text{C}$ .

*Formonitrate of Lead*,  $3\text{CHPbO}^2.\text{PbNO}^3 + \text{H}^2\text{O}$ .—Obtained by dissolving formate of lead in a hot nearly saturated solution of the nitrate, and cooling slowly, in large rhombic crystals, permanent in the air, and sparingly soluble in cold water. (Lucius, Ann. Ch. Pharm. ciii. 113.)

*Formate of Lithium*,  $\text{CHLiO}^2$ .—Rhombic crystals, having the faces  $\infty P. \infty P\infty. P. P\infty. 2P\infty$ . Inclination of  $\infty P : \infty P = 113^\circ 52'$ ;  $P\infty : P\infty$  over the principal



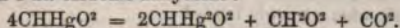
axis =  $106^{\circ} 42'$ ;  $2\tilde{P}\infty : 2\tilde{P}\infty$  over the principal axis =  $91^{\circ} 48'$ . (Handl, Wien. Akad. Ber. xxxii. 252.)

*Formate of Magnesium*,  $\text{CHMgO}^2 + \text{H}^2\text{O}$ .—Crystallises in microscopic rhombic prisms and octahedrons, efflorescing in the air, soluble in 13 pts. water, insoluble in alcohol and ether; gives off its water at  $100^{\circ}\text{C}$ . (Souhay and Groll, J. pr. Chem. lxxvi. 470.)

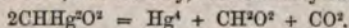
*Formate of Manganese*,  $\text{CHMnO}^2 + \text{H}^2\text{O}$ .—Reddish monoclinic crystals, isomorphous with the following salt, and exhibiting the same faces. Soluble in 15 pts. cold water, insoluble in alcohol. When heated, they give off water and crumble to a white powder.

*Formate of Manganese and Barium*,  $\text{CH}(\text{Mn}; \text{Ba})\text{O}^2 + \text{H}^2\text{O}$ .—This salt, which has the composition of the preceding with an indefinite portion of the manganese replaced by barium, crystallises, on evaporating the mixed solutions of its component salts, in monoclinic crystals exhibiting the combination  $\infty\text{P} . \infty\text{P} . \infty\text{P}\infty . [\infty\text{P}\infty] . + \text{P} . - \text{P} . + 2\text{P}\infty$ . Ratio of axes  $a : b : c = 0.7598 : 1 : 0.9175$ . Angle  $b : c = 82^{\circ} 28'$ ;  $\infty\text{P} : \infty\text{P}$  in the orthodiagonal principal section =  $105^{\circ} 4'$ ;  $\infty\text{P} : + \text{P} = 120^{\circ} 20'$ ;  $\infty\text{P} : \infty\text{P} = 94^{\circ} 33'$ ;  $\infty\text{P} : + 2\text{P}\infty = 112^{\circ} 39'$ ;  $+ \text{P} : + \text{P} = 93^{\circ} 11'$ ;  $- \text{P} : - \text{P} = 109^{\circ} 39'$ . Cleavage distinct parallel to  $\infty\text{P}$ . (Heusser, Pogg. Ann. lxxxiii. 37.)

*Formates of Mercury*.—1. *Mercurous Formate*.  $\text{CHHg}^2\text{O}^2$  or  $\text{CHHhgO}^2$ .—When mercuric oxide is dissolved in cold aqueous formic acid, containing 10 per cent. of the acid ( $\text{CH}^2\text{O}^4$ ), and a gentle heat applied, the solution suddenly solidifies, with intumescence and escape of carbonic anhydride, yielding a micaceous mass; this effect is due to the separation of the mercurous salt formed by the action of the formic acid on the mercuric oxide. At first, a solution of mercuric formate is produced, but on the application of heat, 4 at. of this salt are resolved into 2 at. mercurous formate, 1 at. free formic acid, and 1 at. carbonic anhydride:



As formic acid is set free in this process, the liquid separated from the crystals of the mercurous salt may be again saturated in the cold with mercuric oxide, and then, if gently heated, it will yield another crop of crystals of the mercurous salt. If the mercuric solution be too strongly heated, the crystals turn grey from admixture of mercury, and if a still stronger heat be applied, nothing but metallic mercury is precipitated. The crystals must be dried between bibulous paper at a temperature between  $30^{\circ}$  and  $40^{\circ}\text{C}$ . They are delicate microscopic four and six-sided tables, snow-white with a pearly lustre, and greasy to the touch; their taste is saline at first, but afterwards metallic and astringent. They blacken when exposed to light, especially if moist, and likewise, though more slowly, in the dark. They are decomposed by pressure, or by a heat of  $100^{\circ}$ , into mercury, carbonic anhydride, and formic acid:



When heated in a spoon, they are suddenly decomposed, with a hissing noise, and leave metallic mercury. Their aqueous solution, when continuously heated, gives off carbonic anhydride, and deposits all the mercury in the metallic state, the liquid being converted into a solution of pure formic acid (as shown by the preceding equation). The crystals dissolve in 520 pts. of water at  $17^{\circ}\text{C}$ .; more abundantly, but with incipient decomposition, in warm water; and are insoluble in alcohol and ether. (Göbel, N. Tr. vi. 1, 190; Liebig, Pogg. Ann. iii. 207.)

2. *Mercuric Formate*.—The solution of mercuric oxide in cold dilute formic acid yields, with potash, a precipitate which is yellow at first, and with ammonia a white precipitate; but even if kept cold, it likewise, after a few minutes, deposits crystals of the mercurous salt (Göbel). The finely pulverised oxide dissolves in the cold concentrated acid, forming a syrupy solution, which, if left in vacuo over oil of vitriol, dries up to a white crystallo-granular mass, soluble in water. This mass is likewise converted, by the slightest rise of temperature, into white, acicular mercurous formate, carbonic anhydride being at the same time evolved and formic acid set free. (Liebig.)

*Formate of Methyl*.—See FORMIC ETHERS.

*Formate of Nickel* crystallises in hydrated green needles grouped in tufts; they are very soluble in water, and turn yellow in drying.

*Formates of Potassium*.—1. The *neutral salt*,  $\text{CHKO}^2$ , crystallises with difficulty in white transparent cubes, having a saline bitter taste. They are anhydrous, deliquescent, and very soluble in water. They decrepitate when heated, and at a higher temperature melt to a liquid which solidifies on cooling.

2. *Acid salt*.—A solution of neutral formate of potassium in hot concentrated formic acid, yields, according to Bineau (Ann. Ch. Phys. [3] xix. 291, and xxi. 183), crystalline needles as it cools. The mother-liquor evaporated in vacuo over sulphuric

\* Hg = 100; Hhg = 200.

acid and caustic potash yielded a crystalline mass, part of which was left in *vacuo*, as long as it emitted any odour of formic acid; another portion was dissolved in alcohol and evaporated to dryness in *vacuo*. These three preparations contained formic acid and potash in the proportion indicated by the formula,  $\text{CHKO}^2 \cdot \text{CH}^2\text{O}^2$ , but the first also contained 2.6 per cent. of water, the second 7.6, and the third 11.0 per cent. The salt has a strongly acid taste, and is highly deliquescent. By solution in a large quantity of water and evaporation, it is, for the most part, converted into the neutral salt. When kept for some time in *vacuo*, it gives off part of its acid.

*Formate of Silver*,  $\text{CHAgO}^2$ .—Oxide of silver is instantly reduced by heated formic acid, but the cold acid dissolves it without decomposition; by evaporating the solution, the salt is deposited in transparent rhombohedral crystals. It likewise separates, on mixing moderately strong solutions of nitrate of silver and formate of sodium, in small shining white crystals, which under the microscope exhibit the form of four or six-sided plates. From very strong solutions the salt separates as a curly precipitate.

Formate of silver quickly turns black even in the dark, especially if moist. When heated it is immediately resolved into carbonic anhydride, metallic silver, and formic acid. Potash decomposes it immediately, with evolution of heat. (Liebig.)

*Formates of Sodium*.—1. The *anhydrous neutral salt*,  $\text{CHNaO}^2$ , crystallises in rhombic prisms with bevelled lateral faces, which melt at  $200^\circ \text{C}$ ., are moderately soluble in water, less in alcohol, insoluble in ether (Souhay and Groll, J. pr. Chem. lxxvi. 470). A hydrated salt,  $\text{CHNaO}^2 + \text{H}^2\text{O}$ , was obtained by Göbel, and likewise by Souhay and Groll, in rhombic tables with bevelled lateral faces, or flat four-sided prisms, melting in their water of crystallisation, then giving it off with strong intumescence, and afterwards solidifying to a pearly anhydrous mass. These hydrated crystals are deliquescent and soluble in 2 pts. water. Formate of sodium does not yield any acid distillate when strongly heated.

The solution of this salt is used by Döbereiner to precipitate mercury, silver, gold, palladium, and platinum from their solutions in the metallic state, and thus to separate them from other metals. The dry salt may be used as a reducing agent in blowpipe experiments.

2. The *acid salt*, obtained by dissolving the neutral salt in strong aqueous formic acid, and evaporating in *vacuo*, forms ill-defined crystals, containing acid and base in the proportion represented by the formula  $\text{CHNaO}^2 \cdot \text{CH}^2\text{O}^2$ ; they also contain 7 per cent. of water. The properties of this salt are similar to those of the corresponding potassium-salt. (Bineau.)

*Formate of Strontium*,  $\text{CHSrO}^2 + \text{H}^2\text{O}$ .—The statements of different observers respecting the crystalline form of this salt do not quite agree. According to Kopp (*Krystallographie*, p. 164), it forms crystals belonging to the dimetric or quadratic system, for which  $c = 1.177$ ;  $P : P$  in the terminal edges =  $105^\circ 23'$ ; in the lateral edges =  $118^\circ 30'$ ;  $P\infty : P\infty$  in the terminal edges =  $98^\circ 48'$ ; in the lateral edges  $133^\circ 58'$ . Ordinary combination  $P. \infty P$  with  $2P\infty$  subordinate; or  $P$  with  $P\infty$ , which then occurs hemihedrally, and often as the dominant form. According to Heusser, on the other hand, the salt crystallises in transparent six-sided prisms belonging to the trimetric or rhombic system, with the faces  $\infty P$ ,  $\frac{P}{2}$ ,  $\infty P\infty$ ,  $\frac{P}{2}$ , and

$\frac{2P^2}{2}$ , the two hemihedral forms occurring on opposite sides of the crystal ( $+$   $\frac{P}{2}$  with

$-\frac{2P^2}{2}$ , and  $-\frac{P}{2}$  with  $+\frac{2P^2}{2}$ ), but not being invariably attached to either side.

Ratio of axes  $a : b : c = 0.60761 : 1 : 0.59494$ .<sup>\*</sup> Inclination of  $\infty P : \infty P = 117^\circ 26'$ ;  $P\infty : P\infty$  over the principal axis =  $118^\circ 30'$ . According to Pasteur (Ann. Ch. Phys. [3] xxxi. 67), this salt, though it exhibits non-superposable hemihedral forms (which may be distinguished as *right* and *left*), differs from other salts which exhibit this peculiarity (the dextro- and lævo-tartrates for example) in two respects: first, its solution does not deflect the plane of polarisation of a ray of light; and secondly, on recrystallising either the right or the left variety of the salt, crystals of the opposite kind are always obtained mixed with those of the original variety. But according to E. Jacobsen (Pogg. Ann. cxiii. 493), the development of the hemihedral faces depends altogether on the presence of foreign substances in the solution; a small quantity of free formic acid favours their development, and on recrystallising the salt several times from pure water, they gradually disappear. Jacobsen finds also that carefully selected hemihedral crystals of either variety never yield the opposite variety on recrystallisation. Crystals of the salt prepared with formic acid obtained by the

<sup>\*</sup> As two of these axes differ but slightly in length, the form is very nearly quadratic.



oxidation of starch, when placed so that an obtuse edge of the prism  $\infty P$  is turned to the observer, exhibit for the most part the face  $\frac{P}{2}$  to the left point above (of the observer), whereas crystals of the same salt prepared with formic acid obtained from oxalic acid and glycerin exhibit, for the most part, the face  $\frac{P}{2}$  to the right point above. (Jacobsen.)

Formate of strontium is soluble in water, permanent in the air, and crumbles to a white anhydrous powder when heated.

*Formate of Tetryl.*—See FORMIC ETHERS.

*Formate of Thorinum.*—A solution of hydrate of thorinum in aqueous formic acid yields, by spontaneous evaporation, crystals which form a clear solution in boiling water, but when digested in cold water form an acid solution and leave a basic salt. Alcohol dissolves them but sparingly. (Berzelius.)

*Formates of Tin.*—*Stannous Formate* is sometimes a white insoluble powder, which turns black at first when ignited; sometimes a gelatinous mass which is difficult to dry, and from which alcohol precipitates a white powder. (Arvidson.)

*Stannic Formate.*—Aqueous tetrachloride of tin mixed with formate of sodium does not become turbid till the mixture is heated; it then becomes white and gelatinous, and after a while the precipitate assumes a crystalline character (Liebig.) The acid does not dissolve stannic oxide, even when heated.

*Formates of Uranium.*—1. *Uranous formate.*—Protochloride of uranium yields, with formate of sodium, a green precipitate, which dissolves, with green colour, in excess of the sodium-salt, and does not reappear on further addition of chloride of uranium. But on heating the mixture, it becomes turbid, and deposits a greyish green body containing uranous oxide and formic acid. The colourless liquid filtered from this substance contains a large quantity of formic acid and but little uranium. (Rammelsberg, Pogg. Ann. lix. 34.)

*Uranic Formate.*—Uncrystallisable, glutinous mass, which becomes moist on exposure to the air. (Richter.)

*Formate of Vanadium.*—Hydrated vanadic oxide dissolves in aqueous formic acid, yielding a blue solution, which on evaporation leaves a blue, opaque, saline mass, easily soluble in water. The aqueous solution remains blue if it contains a slight excess of acid; but as this acid evaporates in the air, the solution turns green. (Berzelius.)

*Formate of Zinc*,  $\text{CH}_2\text{ZnO}^2 + \text{H}^2\text{O}$ .—Crystallises by evaporation in monoclinic prisms, isomorphous with the manganese and cadmium salts, and exhibiting the faces  $\infty P$ ,  $\text{oP}$ ,  $+P$ ,  $+2P\infty$ ,  $\infty P\infty$ . Ratio of axes  $a : b : c = 0.76527 : 1 : 0.93430$ . Angle of inclined axes  $= 82^\circ 41'$ ;  $\infty P : \infty P = 104^\circ 32'$ ;  $\text{oP} : +P = 120^\circ 4'$ ;  $\text{oP} : \infty P = 94^\circ 28'$ ;  $\text{oP} : +2P\infty = 112^\circ 14'$ ;  $+P : +P = 93^\circ 17'$  (Heusser). The crystals are permanent in the air, soluble in 24 pts. water at  $19^\circ \text{C}$ ., insoluble in alcohol. By dry distillation they give off pungent inflammable gas, and leave zinc-oxide containing charcoal.

*Formate of Zinc and Barium*,  $\text{CH}(\text{Ba} ; \text{Zn})\text{O}^2$ , forms crystals belonging to the triclinic system. (Heusser.)

**FORMIC ETHERS.** Compounds derived from formic acid by the substitution of an alcohol-radicle for the basic hydrogen. Four of them are known, all derived from alcohols of the series  $\text{C}^n\text{H}^{2n+2}\text{O}$ , viz. the formates of methyl, ethyl, tetryl, and amyl.

*Formate of Amyl*,  $\text{C}^5\text{H}^{12}\text{O}^2 = \text{CH}(\text{C}^5\text{H}^{11})\text{O}^2$ .—This compound, isomeric with capric acid, and with valerate of methyl, butyrate of ethyl, ethylate of tetryl, and propionate of trityl, is obtained by distilling 6 pts. anhydrous formate of sodium, 6 pts. strong sulphuric acid, and 7 pts. amyl alcohol; mixing the distillate with water; washing the separated liquid with solution of carbonate of sodium, then with water; drying over chloride of calcium, and rectifying. It is a colourless mobile liquid, having an agreeable odour, like that of ripe fruits. Specific gravity 0.8743 at  $21^\circ \text{C}$ . (Kopp); 0.8809 at  $16^\circ$ , referred to water at  $4^\circ$  as unity (Mendelejef, Compt. rend. l. 52). Boiling point about  $116^\circ$ . Slightly soluble in water; when kept in vessels containing air it quickly turns acid. (H. Kopp, Ann. Ch. Pharm. lv. 183.)

*Chloramyllic Formate*,  $\text{C}^5\text{H}^{11}\text{ClO}^2$ . Syn. with CHLOROCARBONATE OF AMYL (i. 916).

*Formate of Butyl.*—See FORMATE OF TETRYL.

*Formate of Ethyl*,  $\text{C}^2\text{H}^4\text{O}^2 = \text{CH}(\text{C}^2\text{H}^3)\text{O}^2$ . *Ethylic formate*. *Formic ether*. *Ameisensäther*. *Ameisensäphtha*. (Gm. viii. 482; Gerh. i. 234.)—This ether, isomeric



with propionic acid and acetate of methyl, was discovered by Afzelius of Upsal, in 1777; examined soon afterwards by Bucholz, and by Gehlen, and more exactly by Döbereiner, Liebig, Marchand, Löwig and Weidmann, and H. Kopp. It is obtained by distilling alcohol with strong formic acid, or formate of sodium and sulphuric acid, and by the decomposition of oxalic ether.

*Preparation.*—1. By distilling 7 pts. of dry formate of sodium with a mixture of 6 pts. of highly rectified spirit, and 10 pts. strong sulphuric acid; agitating the distillate, if acid, with magnesia; separating it from alcohol by agitation with water, then decanting the ether and rectifying it over chloride of calcium (Döbereiner). On mixing the three ingredients, heat is evolved sufficient to distil over all the formic ether. The distillate is agitated with an equal volume of milk of lime, and the formic ether evolved as above is dehydrated by chloride of calcium, after separation from the lower stratum, the chloride of calcium being renewed as often as it becomes moist, after which the ether is simply decanted off (Liebig). H. Kopp uses 8 pts. of formate of sodium to 7 pts. alcohol of 88 per cent., and 11 pts. sulphuric acid, conducting the process in other respects in the same manner as Liebig.—2. A mixture of 30 pts. sulphuric acid, 15 pts. water, and 15 pts. highly rectified spirit is poured upon an intimate mixture of 10 pts. starch and 37 pts. very finely pounded manganese, and the whole distilled with gentle ebullition as long as formic ether continues to pass over. A large quantity of chloride of calcium is then dissolved in the distillate, whereby, in the following distillation over the water-bath, the greater part of the water and alcohol is retained, and the liquid which passes over is again rectified with chloride of calcium.

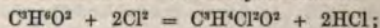
3. Acid oxalate of ethyl distilled with glycerin at 100° C. decomposes similarly to oxalic acid when similarly treated (p. 686), yielding formate of ethyl. The impure ether obtained by prolonged digestion of oxalic acid with alcohol may be used for the purpose. (Church, Phil. Mag. [4] xi. 75.)

4. Formic ether is obtained as a secondary product in the preparation of neutral oxalate of ethyl. When 700 grms. dehydrated oxalic acid (obtained by gently heating a kilogramme of the crystallised acid) are mixed with 750–800 grms. absolute alcohol, or spirit of 97 to 98 per cent., and the mixture distilled in a sand-bath, there is obtained between 145° and 186° C. a distillate containing formate and oxalate of ethyl, together with small quantities of carbonate of ethyl and alcohol, and above 186° pure oxalate of ethyl. The mixture just mentioned may be separated by fractional distillation, the formate of ethyl passing over between 55° and 75°. (Löwig, Ann. Ch. Phys. [3] lxiii. 464; Jahresber. d. Chem. 1861, p. 597.)

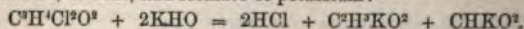
*Properties.*—Formic ether is a thin, transparent and colourless liquid, having a strong agreeable odour, like that of peach-kernels, and a strongly aromatic taste; of specific gravity 0.9157 at 18° C. (Gehlen); 0.9188 at 17°; 0.9984 at 0° (H. Kopp); 0.9577 at 0° (Pierre). Boils at 54° (R. Marchand); at 56°, under a pressure of 27.7" (Döbereiner); at 54.9° with platinum wire immersed in it (H. Kopp); at 52.9° under a pressure of 752 mm. (Pierre); at 54.3 under a pressure of 762 mm. (Andrews). Tension of vapour at 230 = 8.2 inches of mercury (Döbereiner). Vapour-density = 2.593 (Liebig); by calculation (2 vol.) = 2.565. It burns with a blue flame yellow at the edges. It dissolves in 9 pts. water at 18° C., absorbs moisture quickly from the air, and is slowly decomposed thereby into alcohol and formic acid; it must therefore be kept over chloride of calcium. In presence of alkalis the decomposition takes place more quickly. Formic ether mixes in all proportions with alcohol, ether, and wood-spirit, and with many oils, both fixed and volatile. Heated with dry ammonia in sealed tubes, it is converted into formamide (Hofmann, p. 681). With chlorine it yields substitution products (*vid. inf.*).

*Chlorethyllic Formate*,  $C^2H^3ClO^2$ .—Identical with chlorocarbonate of ethyl (i. 916).

*Dichlorethyllic formate*,  $C^2H^2Cl^2O^2 = \begin{matrix} CHO \\ C^2H^2Cl^2 \end{matrix} \} O$ .—Chlorine rapidly attacks formic ether, producing hydrochloric acid and dichlorethyllic formate:



together with formic acid and chloride of ethyl, resulting from the action of the hydrochloric acid on the formic ether. The product is distilled slowly, the temperature not being allowed to exceed 90° C.; at 105° the mixture would turn brown. The residue is poured into water, and the oil which rises to the surface is dried in vacuo. It is soluble in alcohol and ether, but is decomposed by water. Specific gravity = 1.261 at 16° C. It cannot be boiled without decomposition. Aqueous potash attacks it readily, producing chloride, acetate, and formate of potassium:



*Perchlorethyllic formate*,  $C^2Cl^2O^2 = \begin{matrix} CClO \\ C^2Cl^2 \end{matrix} \} O$ .—This compound, produced by the

action of chlorine on formic ether in sunshine, has exactly the same composition, properties, and reactions as perchloromethylic acetate obtained in like manner by the action of chlorine on acetate of methyl (i. 24); in fact the two compounds appear to be identical.

*Formate of Methyl*,  $C^2H^4O^2 = \begin{matrix} CHO \\ CH^3 \end{matrix} \} O$ . *Methylic formate*.—This compound, isomeric with acetic acid, was first obtained in 1835 by Dumas and Peligot (Ann. Ch. Phys. [2] lviii. 48). To prepare it, equal parts of sulphate of methyl and formate of sodium are gently heated in a distillatory apparatus. As soon as the action begins, the mass becomes spontaneously heated, and methylic formate passes over in a nearly pure state into the receiver, which should be well cooled. The methylic formate, which afterwards passes over at a higher temperature, is contaminated with a little methylic sulphate. The distillate thus obtained is rectified over formate of sodium, and then once by itself in a dry retort. In this manner, a perfectly pure product is obtained. This compound is not obtained by distilling wood-spirit and formate of sodium with sulphuric acid.

Formate of methyl is a transparent and colourless liquid, lighter than water, very volatile, and having an ethereal but very pleasant odour. Vapour-density = 2.084 (Dumas and Peligot); by calculation (2 vol.) = 2.08. Boils between  $36^\circ$  and  $38^\circ$  C.; smells like formic ether. (Liebig.)

*Chloromethylic formate*,  $CH^3ClO^2$ .—Identical with chlorocarbonate of methyl (i. 916).

*Perchloromethylic formate*,  $C^2Cl^4O^2 = \begin{matrix} CHO \\ CCl^3 \end{matrix} \} O$ .—To prepare it, perfectly anhydrous methylic formate is placed in a bottle filled with dry chlorine gas, and exposed for some days to the sun (the action, though violent at first, soon diminishes in intensity), till after about fourteen days the colour of the chlorine no longer diminishes. The liquid, which is coloured by free chlorine, is then distilled, the portion which distils over below  $190^\circ$  C. collected apart, and rectified several times, the more volatile portion being each time collected.

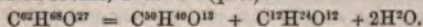
It is a transparent, colourless, very thin liquid, of specific gravity 1.724 at  $10^\circ$  C., boiling at  $180^\circ$  to  $181^\circ$ , and having a strong pungent odour, like that of phosgene. When passed in the state of vapour through a tube heated to  $340^\circ$ — $350^\circ$ , it is converted almost wholly into phosgene gas, with which indeed it is polymeric. Aqueous ammonia acts violently upon it, forming white nacreous trichloracetamide and sal-ammoniac, and probably a third product. *Potash*, even when hot and concentrated, exerts scarcely any decomposing action. *Alcohol* decomposes it, with formation of chlorocarbonate of ethyl; methylic and amylic alcohols form similar products. (Cahours.)

*Formate of Tetryl*,  $C^8H^{10}O^2 = \begin{matrix} CHO \\ C^4H^2 \end{matrix} \} O$ .—Discovered by Wurtz (Ann. Ch. Pharm. xciii. 121). Isomeric with valeric acid, with butyrate of methyl, propionate of ethyl, and acetate of trityl. It is prepared by heating formate of silver with somewhat less than an equivalent quantity of iodide of tetryl in a sealed tube in the water-bath for several hours, then distilling off the volatile product, washing with sodic carbonate, drying over chloride of calcium, and rectifying. It is a fragrant liquid, boiling at about  $100^\circ$  C.

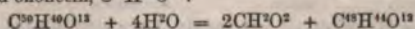
**FORMOMETHYLAL.** See METHYLAL.

**FORMONAPHTHALIDE.** Syn. with NAPHTHYL-FORMAMIDE (p. 681).

**FORMONETIN.**  $C^{50}H^{40}O^{12}$ ? (Hlasiwetz, Wien. Akad. Ber. xv. 142).—A substance obtained, together with glucose, by the action of hot hydrochloric or boiling dilute sulphuric acid on ononin,  $C^{62}H^{40}O^{27}$  (q. v.):



It may be purified and obtained quite white by crystallisation from strong alcohol, or by solution in ammonia and partial precipitation with hydrochloric acid. From the hot alcoholic solution it separates in small crystals. It is nearly insoluble in water and in ether, does not precipitate metallic salts, or colour ferric chloride. Fixed alkalis dissolve it and decompose it at the boiling heat. By sulphuric acid and peroxide of manganese it is coloured violet. By boiling with baryta-water it is resolved into formic acid and ononetin,  $C^{50}H^{40}O^{12}$ :



**FORMONITRILE.** Syn. with HYDROCYANIC ACID (p. 214.)

**FORMULÆ, RATIONAL.**—Chemists are accustomed to distinguish between two different kinds of formulæ; namely, *empirical formulæ* and *rational formulæ*. These terms were first introduced by Berzelius (Jahresber. [1833] xiii. 189; Pogg.



Ann. xxviii. 617; Ann. Ch. Phys. liv. 5; abstr. Ann. Ch. Pharm. vi. 173); the former to denote formulæ which "result immediately from an exact analysis and are invariable:" the latter to denote formulæ which "are designed to give an idea of the two electro-chemically opposite bodies of which the compound is regarded as constituted; that is to say, to render evident the electro-chemical division of the body submitted to analysis." The meaning now attached to these expressions is only so far different from their original meaning as here defined, that, with the growth of new theories of chemical constitution, the signification of rational formulæ has been widened so as no longer to denote the representation of substances on the electro-chemical theory only, but so that a formula which expresses any view whatever respecting the constitution or nature of a substance, beyond what results directly from its analysis, is now called a rational formula.

Empirical formulæ being merely expressions of the results of analysis in terms of the atomic weights of the elements (or more strictly speaking, in terms of the values represented by the elementary symbols: which, however, are always taken in this work as standing for atomic weights), all that is required, in order to fix the empirical formula of any substance, is that the atomic weights of the elements should have been determined, and that the substance itself should have been accurately analysed. Such formulæ, therefore, can never become the subjects of discussion, or of differences of opinion; except, indeed, in cases where the experimental data are incomplete. With rational formulæ, on the other hand, it is very different. A perfect rational formula would amount to a complete statement of the chemical constitution, analogies, and relations of the body which it represents, while the simplest of such formulæ is, by its very nature, an expression of something more than the direct results of experiment. It is obvious, therefore, that the rational formula of any substance must vary with the general theoretical views which from time to time exert the greatest influence in chemical science, and that chemists who hold different opinions with regard to any fundamental point of chemical theory, will assign different rational formulæ to the same bodies. On investigation, however, it will be found that, in very many cases, the different formulæ given to the same substance do not represent distinctly different views of its chemical nature, but that they express the same meaning under different forms. In fact, the question, what is the rational formula of any given substance? resolves itself into these two different parts: (1) what is its chemical function or its place in a general chemical classification? (2) by what formula is this function most suitably expressed? In this article we shall endeavour to show, by the discussion of one or two illustrative examples, the manner in which answers to these questions can be arrived at.

The chemical properties of compounds of the lowest order of complexity appear to depend solely on their chemical composition, and hence the empirical formulæ which express their composition are at the same time the only possible rational formulæ which can be given to them. In more complex compounds, on the other hand, the chemical properties depend, not only on the nature and proportions of their elementary constituents, but also on the mode in which these constituents are combined. Thus acetic acid, lactic acid, formate of methyl, ethyl-carbonic acid, glycollate of methyl, methyl-glycollic acid, glucose, and some other substances, would all give the same results on analysis, and would consequently all be represented by the same empirical formula,  $\text{CH}^{\text{O}}$ . The very different properties exhibited by these bodies, all composed of the same elements united in the same proportions, can be due to nothing but to differences in the mode or order in which these elements are combined in each of them; and although, in most cases, we are far too ignorant of the manner in which the atoms of compound bodies are grouped together, to attempt the expression of it by the arrangement of symbols in our formulæ, still it is possible to indicate to a great extent, by means of rational formulæ, the different chemical characteristics which result from variations in the mode of combination of the same atoms. This, however, can be done only by a comparative method, that is, by selecting a certain number of representative substances, and giving to all other bodies formulæ which shall express the nature of their relations to the substances so selected.

In the article CLASSIFICATION (i. 1010, *et seq.*) it has been shown that the following substances

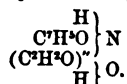
$\text{HCl}$	$\text{H}^{\text{O}}$	$\text{H}^{\text{N}}$	$\text{H}^{\text{C}}$
Hydrochloric acid.	Water.	Ammonia.	Marsh gas.

may be thus taken as typical of all compounds of the simplest order, and that, by the assumption of compound radicles, substances of great complexity may also be compared with them. The rational formulæ adopted in this work amount merely to statements that the substances represented by them are comparable, so far as regards their modes of formation and transformation, with one or other of these fundamental types. Assuming, at present, that this is the best system of rational formulæ, the first question



to be considered — namely, the manner of determining the place of a substance in a general scheme of chemical classification — is seen to be in reality a discussion of the grounds upon which a compound is referred to this or that type, and regarded as containing this or that compound radicle.

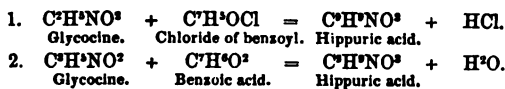
The rules which are practically recognised by chemists in the formation of rational formulæ, will be better explained in relation to particular instances, than by attempting a general exposition of them which should be applicable to all cases. Hippuric acid, for example, is represented by many chemists by the rational formula,



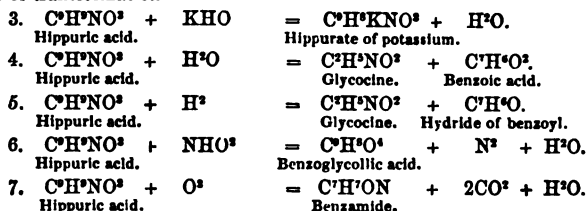
We will proceed to consider in detail the meaning of this expression, and the manner in which it is deduced from the known properties of the substance it represents.

The analysis of hippuric acid leads at once to the empirical formula  $\text{C}^{\text{H}}\text{H}^{\text{O}}\text{NO}^{\text{H}}$ ; and the quantity represented by this expression, is that which results from all reactions in which hippuric acid is formed, as well as that which reacts in all the transformations which this acid is capable of undergoing. This formula therefore represents, not only the composition of hippuric acid, but also its molecular weight. The principal reactions of hippuric acid, at least those which have been chiefly kept in view in deducing the rational formula above given, are expressed by the following equations:

Reactions of formation —



Reactions of transformation —



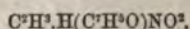
In the first of these equations, that representing the formation of hippuric acid by the action of chloride of benzoyl on glycocine, there is an azotised body and a chloride on each side: on the first side, glycocine and chloride of benzoyl, and on the second, hippuric acid and chloride of hydrogen; and on looking at the composition of these substances, it is seen that the difference between glycocine and hippuric acid is just the same as that between hydrochloric acid and chloride of benzoyl. To express these relations in the rational formula of hippuric acid, it is plain that this formula must represent hippuric acid as bearing the same relation to glycocine that chloride of benzoyl does to chloride of hydrogen; that is, it must represent it as glycocine wherein the radicle  $\text{C}^{\text{H}}\text{H}^{\text{O}}$ , benzoyl, takes the place of an atom of hydrogen. Similarly, equations 2 and 4, which are the converse of each other, show that the relation of hippuric acid to glycocine is the same as that of benzoic acid to water; and equation 5, that it is also the same as that of hydride of benzoyl to hydride of hydrogen: but benzoic acid is to water, and hydride of benzoyl is to hydride of hydrogen, just what chloride of benzoyl is to hydrochloric acid; these last three equations therefore lead to exactly the same rational formula for hippuric acid as the first; that is, to the formula



or an equivalent expression.

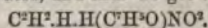
Again, equation 3 shows that hippuric acid contains an atom of hydrogen, which is so far different from the rest that it can be replaced by an atom of another metal, as potassium, while all the other atoms remain in unaltered combination. To express this, we must further break up the formula and write one H separate from the remainder. Here, however, the question arises, how is this result to be combined with the previous one. Are we to represent this exceptional atom of hydrogen as belonging to the original compound glycocine, or to the radicle benzoyl, which we have already admitted as replacing one atom of hydrogen? The answer to this question is obtained by considering the properties of glycocine and chloride of benzoyl, the substances from

which hippuric acid is put together in the reaction represented in equation 1. Glycine contains an atom of hydrogen replaceable by metals; chloride of benzoyl does not: hence the natural conclusion is that the replaceable hydrogen of hippuric acid belongs to the glycine and not to the benzoyl. This is expressed by the formula



whereas the opposite conclusion would be represented by  $\text{C}^2\text{H}^2(\text{C}^2\text{H}^2\text{O}.\text{H})\text{NO}^2$ .

Equation 6 states that an atom of hydrogen and an atom of nitrogen can be removed from hippuric acid and replaced by an atom of oxygen. The hydrogen-atom thus removed appears not to be the one which, as we have already seen, is replaceable by metals: for the product of the reaction, benzoglycollic acid, still contains a similarly replaceable atom of hydrogen. A second H must therefore be separated from the rest in the formula of hippuric acid, and thus we get the expression

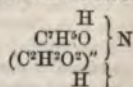


There is reason to believe that the atom of hydrogen in glycine, which can be replaced by metals, owes its special characters to its being in more direct combination with one of the oxygen-atoms of the compound than with the nitrogen: hence, if the conclusion arrived at in the last paragraph but one be admitted, it follows that the radicle  $\text{C}^2\text{H}^2\text{O}$  in hippuric acid is not directly combined with oxygen, but is probably primarily united with the nitrogen. This supposition is strengthened by the reaction represented in equation 7, where, when the other elements are completely oxidised into carbonic anhydride and water, the benzoyl and part of the hydrogen remain united with the nitrogen in the form of benzamide. This can be expressed in the rational formula of hippuric acid by arranging the symbols in such a way as to represent the nitrogen and the group  $\text{C}^2\text{H}^2\text{O}$  as in direct combination; for example, thus—

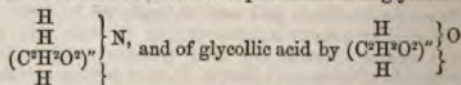


where the atom of hydrogen represented in direct combination with the nitrogen is the one which is displaced, at the same time as the latter, when hippuric acid is acted on by nitrous acid (equation 6), and the second hydrogen-atom written apart from the rest, in the lowest line of the formula, is the one replaceable by metals.

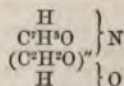
There is still the group of atoms,  $\text{C}^2\text{H}^2\text{O}^2$ , which remains intact throughout all the transformations hitherto considered, except that represented by equation 7, where it is completely oxidised. We might therefore legitimately regard it as a diatomic radicle, and assign to hippuric acid the rational formula



as the one which expresses all its principal transformations. But the adoption of this formula for hippuric acid would involve the representation of glycine by



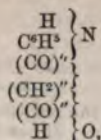
formulae which, though expressing several very important relations of these bodies, not only do not indicate the possible formation of Heintz's diglycolamidic acid,  $\text{C}^2\text{H}^2\text{NO}^4$ , and triglycolamidic acid,  $\text{C}^2\text{H}^2\text{NO}^6$ , or of the diglycollic acid,  $\text{C}^2\text{H}^2\text{O}^3$ , discovered by Wurtz and by Heintz, but conceal the analogy of glycollic acid to lactic acid, which latter cannot be represented with a radicle containing  $\text{O}^2$ , since, by the action of pentachloride of phosphorus, it yields the chloride  $\text{C}^2\text{H}^2\text{OCl}^2$ . For these reasons, a formula in which the radicle  $\text{C}^2\text{H}^2\text{O}^2$  is broken up thus,  $\text{C}^2\text{H}^2\text{O}.\text{O}$ , is a more satisfactory representation of glycine, and consequently of hippuric acid, than that given above. Thus we come finally to the expression



as the ultimate rational formula of hippuric acid.

If, however, we extend our consideration, not merely to the transformations of hippuric acid itself, but also to those of the substances out of which it is built up, or into which it can be decomposed: if, for instance, we take into account the decomposition of benzoic acid into a carbonate and benzene, and of glycine into a carbonate and

methylamine, when distilled with baryta, we must break up this formula still further and write it thus:



or in some equivalent form.

Two points arise from the foregoing discussion which are of sufficient importance to be dwelt upon somewhat more at length. They are, first, the purely relative character of rational formulæ, or their dependence on the particular transformations which they are intended to represent; secondly, the necessity of assigning comparable formulæ to comparable substances.

Rational formulæ being used in the sense which has been indicated in this article, that is, as descriptive only of the bodies to which they are assigned, it is obvious that, if a substance can react in several different ways, it may receive as many distinct rational formulæ, each of which shall be truly descriptive of it relatively to a particular set of transformations; although it can only have one completely rational formula, that is, only one formula indicating all the transformations which it is capable of undergoing. This is nothing more than what we meet with in common language, where, as we know, several distinct partial descriptions of the same object may be each of them quite accurate as far as they go, although there cannot be more than one complete description of it. This is almost too simple a matter to need to be specially pointed out, were it not that some chemists maintain that the same substance cannot have more than one rational formula. For instance, in the *Annalen der Chemie und Pharmacie*, vol. cxiii. pp. 225, 226 (February, 1860), we find the following passage in reference to the two formulæ  $\left\{ \begin{array}{c} \text{C}^3\text{H}^4\text{O} \\ \text{C}^2\text{H}^3 \end{array} \right\} \text{O}$  and  $\left\{ \begin{array}{c} \text{C}^3\text{H}^4\text{ClO} \\ \text{C}^2\text{H}^3 \end{array} \right\} \text{O}$ , which Wurtz, in order to express the

different ways in which that body reacts, had assigned to the product of the action of alcohol on chloride of lactyl:

"If two isomeric bodies are recognised as distinct substances because they contain their proximate constituents grouped in different ways; if further the rational constitution, as distinguished from the empirical constitution, is that which indicates the proximate constituents of a compound together with the part which they play therein; and if finally the rational formula is the symbolic expression of the conception which we form to ourselves, at any given time, respecting the rational constitution of a body, it is not possible that, as Wurtz supposes in the case of chloropropionic ether, a compound can have two rational formulæ at the same time; that is, that it can be variously constituted. No one will share the opinion that the chloropropionic acid which produces lactic acid is not identical, but merely isomeric, with that which is converted by hydrogen into propionic acid."

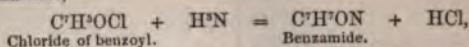
"... To advocate at one time two different rational formulæ for the same compound, that is, to pretend that it contains now one group of atoms, and now another as its proximate constituents, and contains them perhaps differently combined together, as is expressed by Wurtz's two formulæ for chloropropionic ether, is to assert an impossibility."

On examining these quotations, it will be seen that the use of rational formulæ which is contemplated by them is not quite that which has been explained in this article. The author plainly regards rational formulæ as symbolic expressions of suppositions respecting the constitution of compounds, whereby it is sought to explain their chemical properties. Regarding the reactions of compound bodies as determined, not only by the nature of their elements, but also by the way in which their constituent atoms are united, he considers that rational formulæ ought to represent the ultimate structure of bodies, and thus show why they exhibit the particular properties by which they are characterised. If we had the means of ascertaining with certainty the constitution of bodies, there can be no question that formulæ by which it was expressed would be the best rational chemical formulæ, and that of such formulæ, only one could be true for each substance; but, since our only mode of learning how bodies are constituted is by studying the reactions by which they are formed and transformed, it seems the safest course to be satisfied, for the present, with formulæ which simply indicate what these reactions are, resting assured that the best way of arriving at a knowledge of their cause is by endeavouring to attain a distinct and complete conception of their manner.

When considering any reaction for the purpose of deducing from it a rational



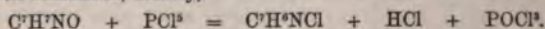
formula for the bodies which take part in it, we have always to distinguish between the constituents which are unaffected by the reaction and those which are added, separated, or replaced by others. Thus when chloride of benzoyl acts on ammonia, producing benzamide,



we have the group  $\text{C}^{\text{H}}\text{H}^{\text{O}}$  common to the reagent and to the product, while Cl in the former is replaced by  $\text{H}^{\text{N}}$  in the latter. It has been explained in the article CLASSIFICATION (i. 1014, 1015) that the group which remains constant throughout a reaction is the radicle of the substances concerned in it, while the atoms that are affected by the reaction are those which serve to characterise the type of the reagent and product respectively. In the rational formula of any substance, the radicle expresses its genetic

relations, and the type its chemical function. In the formula  $\left. \begin{array}{c} \text{C}^{\text{H}}\text{H}^{\text{O}} \\ \text{H} \end{array} \right\} \text{N}$ , for benza-

amide, the radicle  $\text{C}^{\text{H}}\text{H}^{\text{O}}$  indicates that the substance belongs to the same chemical family as benzoic acid, oil of bitter almonds, and chloride of benzoyl; while the symbol of nitrogen outside the bracket, and the two Hs within, denote that its chemical function is that of a primary monamide (AMIDES, i. 169). This formula, however, plainly does not indicate the possibility of a reaction such as that of pentachloride of phosphorus on benzamide, namely,



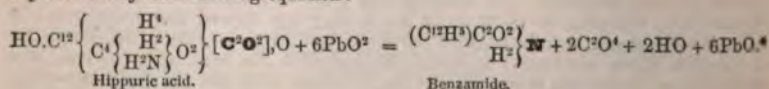
To obtain a formula which shall do so, we must, as before, distinguish between the atoms which are affected by the reaction and those which remain in unaltered combination; we thus get from this equation the rational formula for benzamide,  $\left. \begin{array}{c} \text{C}^{\text{H}}\text{H}^{\text{O}}\text{N} \\ \text{H} \end{array} \right\} \text{O}$ , which represents it as the hydrate of the radicle  $\text{C}^{\text{H}}\text{H}^{\text{O}}\text{N}$ .

The consideration of two different reactions thus leads to the representation of benzamide at one time as an amide, at another as a hydrate, but it is possible to express both these reactions by a single rational formula, if we represent benzamide as

at once an amide and a hydrate. This is done by the formula  $\left( \left. \begin{array}{c} \text{H} \\ \text{C}^{\text{H}}\text{H}^{\text{O}} \end{array} \right\} \text{N} \right)^{\text{m}} \left. \begin{array}{c} \text{H} \\ \text{H}^{\text{O}} \end{array} \right\} \text{O}$ , where  $\text{C}^{\text{H}}\text{H}^{\text{O}}$ , the group of atoms which remains unaltered throughout both reactions, is the radicle, and the type  $\left. \begin{array}{c} \text{H}^{\text{N}} \\ \text{H}^{\text{O}} \end{array} \right\}$ .

It is important to notice here that a formula derived from a simple type can only express reactions of the kind which is characteristic of that type, and that, as soon as we have to express more than one kind of reaction by the same formula, we must make use of a complex type. It is obvious, however, that complication of type involves simplification of radicle, and *vice versa*; so that a formula expressing all the reactions in which a given substance could possibly take part, whether as reagent or product, would be one containing only radicles of the greatest possible simplicity; that is, consisting of single elementary atoms. All rational formulæ containing compound radicles are necessarily partial, for they cannot express any reactions in which the constituents of those radicles are separated from each other. Such formulæ are nevertheless, the most commonly useful, for it is more frequently necessary to point out the relations of one substance to others of a comparable degree of complexity, than to indicate the reactions by which it can be put together from its constituent atoms, or by which these can all be separated from each other. (See further, *Preliminary Report on Organic Chemistry*, by G. C. Foster. Reports of British Associat. for 1859, pp. 7-11.)

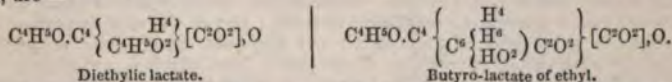
The second point which, as has been stated, arises out of the discussion of the formula of hippuric acid, is the necessity of giving comparable formulæ to comparable substances, or of adopting a uniform system of rational notation; that is, always expressing similar reactions in the same way. What is meant will become more clearly intelligible by an example of that which, we contend, is an illogical and inconsistent use of formulæ. In Kolbe's *Lehrbuch der organischen Chemie* (Braunschweig, 1860, ii. p. 117), the decomposition of hippuric acid, when boiled with binocide of lead, is represented by the following equation:



\* In this equation, and in what follows in reference to it, H=1, O=8, C=6, &c.

Hippuric acid is here represented as benzoic acid,  $\text{HO} \cdot (\text{C}^{12}\text{H}^5)[\text{C}^2\text{O}^2] \cdot \text{O}$  (according to Kolbe), wherein amido-acetoxyl,  $\text{C}^4 \left\{ \begin{smallmatrix} \text{H}^2 \\ \text{H}^2\text{N} \end{smallmatrix} \right\} \text{O}^2$  (the radicle assumed by Kolbe to exist in glycocine or amido-acetic acid), replaces one atom of hydrogen; while benzamide is represented as ammonia in which an atom of hydrogen is replaced by benzoyl, although, as we have already seen, hippuric acid bears exactly the same relation to glycocine that benzamide does to ammonia. Chloride of benzoyl reacts on glycocine exactly as it does on ammonia, forming in the one case hippuric acid, in the other benzamide; yet the above formulæ represent the products as related to the reagents quite differently in the two reactions. In the first, substitution is represented as having taken place within the radicle  $(\text{C}^{12}\text{H}^5)\text{C}^2\text{O}^2$ ; in the second, this radicle is represented as being itself substituted for hydrogen.

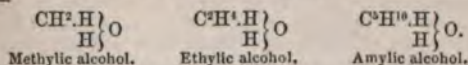
The same chemist furnishes us with another example of the illogical use of formulæ, in the expressions by which he represents the products of the action of chloropropionic ether (Wurtz's *ether chlorolactique*) on ethylate of sodium and on butyrate of sodium respectively. The reaction is in both cases perfectly similar, and may be described as the combination of the reagents, with elimination of chloride of sodium. Kolbe nevertheless formulates the first product, diethylic lactate, as chloropropionic ether wherein the chlorine is replaced by binoxide of ethyl, but represents the second, butyro-lactate of ethyl, as chloropropionic ether wherein the chlorine is replaced — not by binoxide of butyryl but—by butyryl in which binoxide of hydrogen is substituted for an atom of hydrogen. The formulæ in question, retaining the atomic weights used by the author, are—



This incorrect use of rational formulæ caused Kolbe to predict that butyro-lactate of ethyl would undergo a decomposition, when boiled with dilute hydrochloric acid, different from that which is found actually to occur. (See Ann. Ch. Pharm. cxiii. 235.)

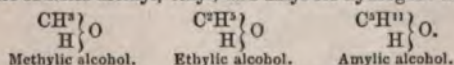
We have drawn attention to these examples of the wrong use of formulæ, because it is necessary to bear clearly in mind that, whatever system of rational formulæ we may prefer, and whatever may be our opinions as to what can and what ought to be expressed by them, the language of chemical symbols obeys the same laws as all other languages, and ceases to have value or meaning when dissimilar expressions are used to represent identical relations.

When it has been ascertained by the study of their reactions, that two or more substances are of allied constitution, there are two ways in which the relations between them may be expressed by rational formulæ. In the first, or *additive* system, substances of similar function are represented as containing, as a common constituent, the first term of the series to which they belong, united in each of them to a different additional group. In this system of formulæ, methylic, ethylic, and amylic alcohols would be respectively represented as water combined with methylene, with ethylene, and with amylene: thus—

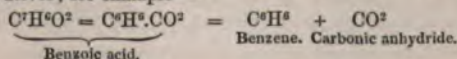


In these formulæ, the constant constituent denotes the chemical function; the variable addition, or *copula*, characterises the family to which the substance belongs.

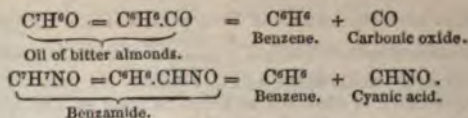
Formulæ of the second kind may be called *substitutive*. They are such as those commonly employed in this work. In this system, a series of allied bodies are not represented as containing the first term as such, but as derived from it by substitution. Thus, the three alcohols above mentioned are represented as derived from water by the substitution of the radicles methyl, ethyl, and amyl for hydrogen: namely—



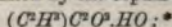
The earliest rational formulæ used in organic chemistry, namely, those by which Dumas and Boullay (Ann. Ch. Phys. xxxvii. 15, 1828) represented the constitution of the compound ethers, were additive; and formulæ of this kind long remained in almost exclusive use by chemists of the French school. Similar formulæ were proposed by Mitscherlich (Ann. Ch. Phys. lv. 41, 1834; Ann. Pharm. ix. 39) for benzoic acid and some of its derivatives; for example—







All such formulæ, however, were rejected by Berzelius and his followers, on the ground that they represented a mode of combination unknown in mineral chemistry (see Pogg. Ann. xlvii. 289, 1838); until, in order to be able to represent the constitution of trichloroacetic acid as in harmony with the electro-chemical theory, Berzelius himself (*Lehrb. d. Chemie*, 5<sup>te</sup> Aufl. i. 709) gave an additive formula to acetic acid, representing it as oxalic acid modified by the copula methyl: thus—



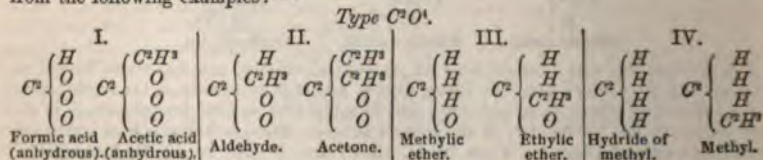
and the same idea was extended by Kolbe, in 1848 (*Handwörterb.* iii. 177 [article, *Formeln, chemische*]; also Ann. Ch. Pharm. lxxv. 288), to the whole series of acids homologous with acetic acid; and by Berzelius to the organic alkaloïds, which he regarded as formed by the combination of ammonia with various copulae.

It is obvious, that every additive formula can be easily transformed into an equivalent substitutive formula; thus, for instance, Wurtz's formula for acetic acid,  $\text{C}^2(\text{C}^{\text{H}})^2\text{C}^{\text{O}}\text{HO}$  (Ann. Ch. Phys. [3] xxx. 502), which represents it as formic acid wherein methyl is substituted for hydrogen, is the substitutive equivalent of Berzelius's additive formula. All relations of composition and function can therefore be expressed almost equally well in either system. Nevertheless, there are some reasons for giving the preference in general to substitutive formulæ. One of the most important is, that by using the latter kind of formulæ, we can represent entire series (of homologous bodies, for example) by expressions of the same form, which is not always possible with additive formulæ. Thus, if we represent succinic acid as derived from two mole-

cules of water by the substitution of the radicle  $\text{C}^{\text{H}}\text{O}^2$  for  $\text{H}^2$ ,  $\frac{\text{C}^{\text{H}}\text{O}^2}{\text{H}^2}\text{O}^2$ , we can express all the homologous acids by similar formulæ; for instance, malonic acid =  $\frac{\text{C}^{\text{H}}\text{O}^2}{\text{H}^2}\text{O}^2$ , oxalic acid =  $\frac{\text{C}^{\text{O}}}{\text{H}^2}\text{O}^2$ ; but if we write succinic acid thus—

$\frac{\text{C}^{\text{H}}\text{O}^2.\text{H}^2}{\text{H}^2}\text{O}^2$ , or, as two molecules of water to which the copula  $\text{C}^{\text{H}}\text{O}^2$  is added, it becomes impossible to represent oxalic acid by a comparable formula. Another somewhat similar objection to the use of additive formulæ is, that they are not applicable to inorganic and organic bodies alike. Thus, although we can easily express the relations between methylic and ethylic alcohols, or between ethylic alcohol, chloride of ethyl, and ethylamine by means of such formulæ, we cannot indicate the relation which exists between the alcohols and such bodies as hydrate of potassium; formulæ, however, which represent all these compounds as derived from water by the substitution of various radicles for one atom of hydrogen, render their mutual relations at once apparent.

A system of formulæ, partly additive and partly substitutive, is employed by Professor Kolbe. One or two specimens of his formulæ have already been given in this article. The chief points of difference between them and the formulæ employed in this work are that oxygen-compounds are employed, instead of hydrogen-compounds, as the types or standards of comparison, and that compounds containing only carbon, hydrogen, and oxygen are referred to the type  $\text{C}^2\text{O}^4$  (equivalent to  $\text{CH}^4$ ) instead of to the type  $\text{H}^4\text{O}$ . This mode of formulating organic compounds is an extension of the views advanced by Frankland (Ann. Ch. Pharm. lxxxv. 364) regarding the constitution of the so-called organo-metallic bodies, and was in fact first suggested by the last-named chemist (see Proc. Roy. Inst. ii. 540, May 28, 1858). The manner of representing some of the most important classes of compounds, on this system, will be understood from the following examples:—



The acids of the acetic series are represented as formed from carbonic anhydride by the substitution of hydrogen or an alcohol-radicle for one equivalent of oxygen; the

\* A similar formula for acetic acid had been previously suggested by Matteucci (Ann. Ch. Phys. iii. 134, 1833.)



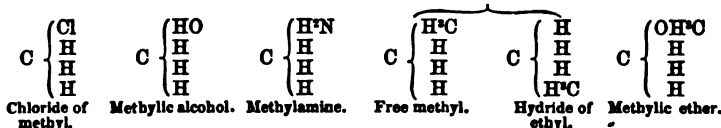
aldehydes are represented as formed by the replacement of one equivalent of oxygen by hydrogen and one by an alcohol-radicle, and the ketones by the replacement of two equivalents of oxygen by alcohol-radicles. The replacement of three equivalents of oxygen by hydrogen or by alcohol-radicles gives the simple ethers, and the similar replacement of all the oxygen gives the alcohol-radicles as they exist in the free state, or their hydrides.

There are some relations of these substances which can be brought out more distinctly by comparing them to a carbon-compound as type than by referring them to the types  $H^2O$  and  $H^2$ , as is done in the formulæ commonly used in this work; but the use of an oxygen-compound, such as carbonic anhydride, for this purpose, involves the occurrence of fractions of an atom of oxygen in the formulæ of all substances represented as formed by the substitution of an odd number of atoms of hydrogen, or of any monatomic radicle, for its equivalent of oxygen. This will be seen by referring to the formulæ of the acids homologous with acetic acid, and to those of the simple ethers as given above.

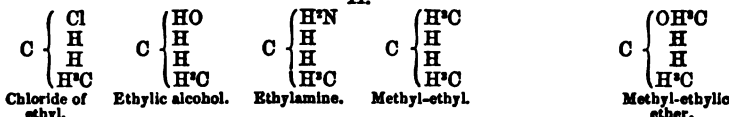
All the advantages of formulæ of this kind, without the inconsistency of being obliged to introduce half-atoms, may be secured by representing the compounds in question as derivatives of the type  $CH^4$ . A few examples will be sufficient to show how this may be carried out.

### Type $CH^4$ .

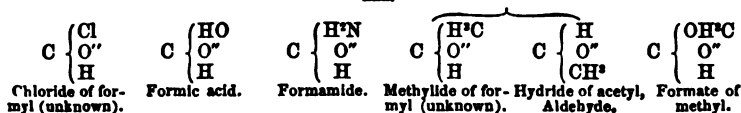
#### I.



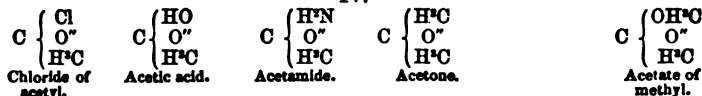
#### II.



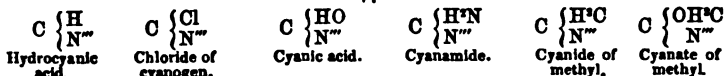
#### III.



#### IV.



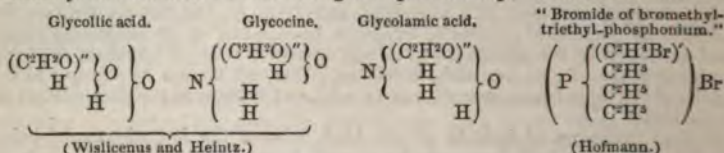
#### V.



These formulæ express very clearly the relations of composition of the bodies represented by them; and if we possessed any reagent whereby we could replace carbon by other elements, in the same way that chloride and sulphide of phosphorus enable us to replace oxygen by chlorine and sulphur respectively, the transformations effected by it would be best represented by formulæ of this kind: just in the same sense that the formulæ  $\begin{Bmatrix} C^2H^2O \\ H \end{Bmatrix} O$  = acetic acid,  $C^2H^2O.Cl$  = chloride of acetyl, best correspond to the reactions produced by pentachloride of phosphorus. Comparatively few transformations, however, are as yet known which are better expressed by formulæ derived from the type  $CH^4$ , than by those derived from the types  $HCl$ ,  $H^2O$ , and  $H^2N$ , though, intrinsically, one set of formulæ is just as admissible, and just as logical, as the other.

With regard to the rational formulæ of polyatomic compounds, another question has arisen, which is one of form rather than of the meaning to be expressed. In many diatomic and polyatomic compounds, a certain dissymmetry of properties, if we may use

the expression, may be observed; that is, the same reaction can be produced twice or oftener with one molecule of the substance, but it does not take place with exactly the same facility each time. Thus, glycollic and lactic acids contain two atoms of hydrogen capable of being replaced by alcohol-radicles; but the replacement of only one atom can be effected by the ordinary processes of etherification, the second atom can only be replaced by indirect means. In order to express this peculiarity in the formulæ of these and similar substances, several chemists have adopted the expedient of writing one of the replaceable atoms as though it were combined with the remaining elements differently from the rest. The following examples will explain what is meant:



So long as such formulæ are understood to be descriptive merely, they are perfectly admissible, and may often be employed with advantage, as indicating more exactly than the ordinary polyatomic formulæ—such as  $\left( \begin{array}{c} \text{C}^2\text{H}^2\text{O} \\ \text{H}^2 \end{array} \right) \text{O}^2 =$  glycollic acid,  $\left( \begin{array}{c} \text{C}^2\text{H}^2\text{O} \\ \text{H}^2 \end{array} \right) \text{N}$  = glycicine or glycolamic acid—the properties of the substances to which they are assigned; but, if they are taken as actual expressions of the peculiarities of constitution on which these properties depend, they come to be of questionable service. For the unequal facility with which the two replaceable atoms of hydrogen in glycollic acid, for instance, can be replaced, is no proof that they are not combined in the same way. It may very well be that these two atoms, or even all four atoms of hydrogen, are perfectly equivalent to each other, so long as the original compound remains intact; but that, as soon as one atom is replaced by another element or radicle, the equilibrium of the whole group is modified in such a way that the similar replacement of another atom cannot be effected with the same ease.

On the other hand, however, there are facts which point to a real difference between one of the four units of combining capacity of an atom of carbon and the other three. Thus, for instance, the chloride of methyl formed by the action of chlorine on marsh-gas differs in some of its properties from that produced by the action of hydrochloric acid on methylic alcohol, or by the decomposition of trichloride of cacodyl; a fact which it is difficult to explain, except by supposing it to depend on the different position of the chlorine atom in the two compounds. Some very interesting and important consequences of this supposition have been developed by Butlerow (*Zeitschr. Chem. Pharm.* iv. 549); and by Erlenmeyer (*ibid.* v. 18). Should it, on further investigation, appear to be well founded, some expression of the facts upon which it is based will, of course, have to be given in our rational formulæ; and, in formulæ derived from the type  $\text{CH}^4$ , this may easily be done. (See the formulæ of methyl and hydride of ethyl, methylide of formyl and hydride of acetyl on p. 703.)

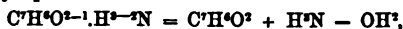
In conclusion, we must mention, for the sake of their historical interest, the *Synoptical formulæ* of Gerhardt and Chancel, although this mode of notation is probably no longer employed by any chemist. These formulæ may be considered as abbreviated modes of writing the equations of formation of the bodies which they represent. Thus, for instance, sulphobenzidic acid, formed by the union of one molecule of sulphuric acid and one molecule of benzene, with elimination of a molecule of water, may be represented by the synoptical formula  $\text{SO}^{4-1} \left\{ \begin{array}{c} \text{H.C}^6\text{H}^4-2 \\ \text{H} \end{array} \right\}$ , equivalent to the equation of formation  $\text{SO}^4\text{C}^6\text{H}^4 = \text{SO}^4\text{H}^2 + \text{C}^6\text{H}^6 - \text{OH}^2$ ; similarly sulphobenzide may be represented by the synoptical formula  $\text{SO}^{4-2} \left\{ \begin{array}{c} \text{H.C}^6\text{H}^4-2 \\ \text{H.C}^6\text{H}^4-2 \end{array} \right\}$ , equivalent to the expression  $\text{SO}^4\text{H}^2 + 2\text{C}^6\text{H}^6 - 2\text{OH}^2$ . The following are additional examples, extracted from Gerhardt and Chancel's paper (*Comptes rendus des travaux chimiques*, vii. 65; March, 1851), together with the more detailed expressions to which they are equivalent:

Names of substances.	Synoptical formulæ.	Equivalent expressions.
Carbamic acid . . .	$\text{CO}^{3-1} \left\{ \begin{array}{c} \text{H.H}^2-2\text{N} \\ \text{H} \end{array} \right\}$	$\text{CO}^3\text{H}^2 + \text{H}^2\text{N} - \text{OH}^2$
Urea (carbamide) . . .	$\text{CO}^{3-2} \left\{ \begin{array}{c} \text{H.H}^2-2\text{N} \\ \text{H.H}^2-2\text{N} \end{array} \right\}$	$\text{CO}^3\text{H}^2 + 2\text{H}^2\text{N} - 2\text{OH}^2$
Carbanilic acid . . .	$\text{CO}^{3-1} \left\{ \begin{array}{c} \text{H.C}^6\text{H}^4-2\text{N} \\ \text{H} \end{array} \right\}$	$\text{CO}^3\text{H}^2 + \text{C}^6\text{H}^4\text{N} - \text{OH}^2$

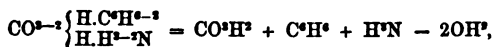
Carbanilide . . . . .	$\text{CO}^{2-2} \left\{ \begin{array}{l} \text{H.C}^{\text{H}^2-2}\text{N} \\ \text{H.C}^{\text{H}^2-2}\text{N} \end{array} \right.$	$\text{CO}^2\text{H}^2 + 2\text{C}^2\text{H}^2\text{N} - 2\text{OH}^2$
Carbovinic acid . . . . .	$\text{CO}^{2-1} \left\{ \begin{array}{l} \text{H.C}^2\text{H}^{4-2}\text{O} \\ \text{H} \end{array} \right.$	$\text{CO}^2\text{H}^2 + \text{C}^2\text{H}^4\text{O} - \text{OH}^2$
Carbonate of ethyl . . . . .	$\text{CO}^{2-2} \left\{ \begin{array}{l} \text{H.C}^2\text{H}^{4-2}\text{O} \\ \text{H.C}^2\text{H}^{4-2}\text{O} \end{array} \right.$	$\text{CO}^2\text{H}^2 + 2\text{C}^2\text{H}^4\text{O} - 2\text{OH}^2$
Urothane (carbamate of ethyl)	$\text{CO}^{2-2} \left\{ \begin{array}{l} \text{H.C}^2\text{H}^{4-2}\text{O} \\ \text{H}^2-2\text{N} \end{array} \right.$	$\text{CO}^2\text{H}^2 + \text{C}^2\text{H}^4\text{O} + \text{H}^2\text{N} - 2\text{OH}^2$
Acetic acid . . . . .	$\text{CO}^{2-1} \left\{ \begin{array}{l} \text{H.CH}^{4-2} \\ \text{H} \end{array} \right.$	$\text{CO}^2\text{H}^2 + \text{CH}^4 - \text{OH}^2$
Acetone . . . . .	$\text{CO}^{2-2} \left\{ \begin{array}{l} \text{H.CH}^{4-2} \\ \text{H.CH}^{4-2} \end{array} \right.$	$\text{CO}^2\text{H}^2 + 2\text{CH}^4 - 2\text{OH}^2$

It will be observed that the formulæ here given for acetic acid and acetone do not correspond to any process then known by which these bodies could be formed; but, if taken in an analytical, instead of in a synthetical sense, they indicate the manner in which these substances are decomposed when distilled with alkaline hydrates. The formulæ of urea, carbanilic acid, and carbanilide, must likewise be taken in an analytical sense merely.

Each synoptical formula can obviously express only one mode of formation or decomposition of a substance, and hence cannot be regarded as a general expression of its reactions; thus, considering the formation of benzamide from benzoate of ammonia by loss of water, and its decomposition into benzoic acid and ammonia, we may represent it by the synoptical formula



or



but neither of these expressions would indicate its formation by the action of chloride of benzoyl on ammonia. It is probably this want of generality which has prevented formulæ of this kind from coming into general use.—G. C. F.

**FORMYL.** CHO.—The radicle of formic acid and its derivatives, being the first term in the series of acid radicles  $\text{C}^2\text{H}^{2n-2}\text{O}$ . The same term was formerly applied to the radicle CH: hence the names *chloroform*, *formonitrile*, &c.; but it is better to denote this hydrocarbon-radicle by the term *xylyl*.

**FORMYLIA, FORMYLAMINE.** Names applied to the first base obtained by the action of ammonia on bromide of ethylene, and originally supposed to have the composition  $\text{CH}_2\text{H}^2\text{N}$ . (See *ETHYLENE-BASES*, ii. 687.)

**FORMYLINE.** The name given by Rochleder (Ann. Ch. Pharm. lxi. 120) to a base which he obtained by the decomposition of caffeine, and supposed to have the composition  $\text{CH}^2\text{N}$ . Wurtz, however, showed (Compt. rend. xxx. 9), that it is nothing but methylamine.

**FORMYL-DIPHENYL-DIAMINE.** See PHENYLAMINES.

**FORSTERITE.** A white or colourless translucent chrysolite occurring in small crystals on Vesuvius.

**FORRESINIC ACID.** The name given by Bastick (Pharm. J. Trans. viii. 339) to the acid resin produced by the action of nitric acid on copalin or Highgate resin (ii. 21).

**FOURNETITE.** A variety of tetrahedrite from Beaujeu (Rhône) and Val Godemar (Hautes Alpes), consisting, according to Mène (Compt. rend. li. 463; i. 311), of  $3\text{Cu}^2\text{S}.\text{Sb}_2\text{S}_3$ , together with  $\text{Pb}^2\text{S}$  and  $\text{Fe}^2\text{As}$  (in the mineral from Beaujeu) or  $\text{Fe}^2\text{As}^2$  (in that from Val Godemar).

**FWLERITE.** Crystallised rhodonite from Franklin, New Jersey. (See RHODONITE.)

**FOYATITE.** A rock resembling syenite, which forms the mountains Foya and Picota in the Monchique range (Algarvia in Portugal), and consists mainly of orthoclase associated with elæolite and hornblende, and as accessory constituents, titanite, hexagonal pinchbeck-brown mica, magnetic iron-ore and iron-pyrites. Its structure is coarse to fine grained, also porphyritic. (Blum, Jahrb. Min. 1861, p. 426.)

**FRACTURE OF MINERALS.** The uneven or irregular surface produced by breaking amorphous minerals is distinguished, as:

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Z. Z.



1. *Conchoidal*, when the mineral breaks with curved surfaces like those of a shell; this kind of fracture is seen in flint.

2. *Uneven*, when the surface of fracture is rough, with numerous small elevations and depressions.

3. *Splintery*, when the broken surface exhibits protruding points.

4. *Hackly*, when the elevations are sharp and jagged as in broken iron.

The fracture is, for the most part, of constant character in the same mineral species; but the same kind of fracture, especially the uneven and the splintery, is common to so many minerals, as to render these characters of comparatively little value in determining species.

**FRAGARIA.** *Strawberry.*—Buignet (J. Pharm. [3] xxxvi. 81, 170) has examined several varieties of strawberry, and finds that the free acid contained in them is malic acid, and that the sugar consists of cane sugar, dextroglucose and levoglucose in varying proportions. The cane-sugar, which is contained in cells distinct from those which contain the malic acid, appears to be the sugar first formed in the fruit, and to be more or less converted into the other kinds of sugar during the osmotic mixture of the several liquids contained in the cells.

**FRADRONITE.** A rock occurring near Lozère in the western range of the Cévennes, where it often traverses the granite and slates. It usually appears to consist of a dark green feldspathic basis, mixed with a large quantity of bronze-like mica. The most ordinary variety contains in 100 parts:

Felspar and Mica.	SiO <sub>2</sub>	Al <sup>2</sup> O <sub>3</sub>	Mg <sup>2</sup> O	Fe <sup>2</sup> O	H <sub>2</sub> O	Fe <sup>2</sup> CO <sub>3</sub>	Ca <sup>2</sup> CO <sub>3</sub>
50.0	15.0	5.0	3.4	4.0	1.5	17.5	3.6

The constituents bracketed together seem to consist of a mineral resembling chlorite which serves to cement together the felspar and mica; calcspar and spathic iron are also present, but do not appear to be essential constituents of the formation. (Lan, Ann. Min. [5] vi. 412.)

**FRANCOLITE.** A fluorapatite occurring in spherical aggregations at Wheal Francis, near Tavistock in Devonshire (i. 349).

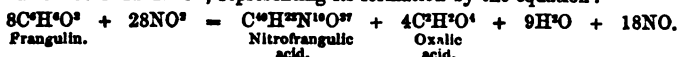
**FRANGULIN.** C<sup>9</sup>H<sup>10</sup>O<sup>3</sup> (A. Casselmann, Ann. Ch. Pharm. civ. 77; Jahresb. d. Chem. 1857, p. 522).—A yellow crystallisable colouring matter, contained in the bark of the berry-bearing alder (*Rhamnus Frangula*). It is accompanied by an amorphous resinous yellow substance, and occurs most abundantly in the bark of the older branches, that of the younger branches containing a larger proportion of the resinous constituent. The yellow substance, called *Rhamnoxanthin*, obtained by Buchner (Jahresber. 1853, p. 536) from the root bark of the same shrub was, according to Casselmann, impure frangulin.

*Preparation.*—1. The comminuted bark is repeatedly exhausted with ammoniacal water at the boiling heat; the dark red extracts are mixed with hydrochloric acid; and the slowly-depositing, brown-black precipitates thereby produced are washed, and treated at the boiling heat with alcohol of 80 per cent., with addition of neutral acetate of lead, nearly the whole then dissolving and forming a brownish-yellow solution. This solution is further treated with neutral acetate of lead to precipitate tannin, &c.; the hot filtered liquid is mixed with water till it becomes strongly turbid, then heated till the turbidity disappears; the liquid is left to itself for a week; and the frangulin which separates is purified by repeated crystallisation from boiling alcohol. —2. The alcoholic solution, after being filtered from the precipitate produced by neutral acetate of lead, is shaken up with hydrate or with basic acetate of lead, the precipitate, which contains all the frangulin, is suspended in very dilute alcohol and decomposed by sulphydric acid; the sulphide of lead is exhausted by boiling alcohol, which leaves the greater part of the resinous matter undissolved; the solution is diluted with water; and the frangulin which separates is repeatedly crystallised from alcohol.

Pure frangulin forms lemon-yellow crystalline masses (composed of microscopic square plates), having a dull, silky lustre, tasteless and inodorous. It melts at about 249° C., and at the same temperature begins to sublime with partial decomposition in golden-yellow microscopic needles. It is insoluble in water, soluble in 160 pts. of warm alcohol of 80 per cent., nearly insoluble in cold alcohol, sparingly soluble in boiling ether, soluble in hot fixed oils, benzene, and oil of turpentine. When dried at 100° C., it has the composition indicated by the formula above given.

Frangulin does not appear to form definite compounds with *bases*. It dissolves with purple-red colour in *alkalis*, and is precipitated yellow by *acids*. It is not precipitated by metallic salts. With strong *sulphuric acid*, it forms at ordinary temperatures a dark-red solution, which becomes brown when heated, and from which it is precipi-

tated by water. Strong *nitric acid* dissolves it at the boiling heat without decomposition. Fuming *nitric acid* dissolves it, with evolution of nitrous vapours, forming oxalic acid, and if the action has not been too violent, or the temperature too high, another acid called *nitrofrangulic acid*, to which Casselmann assigns the formula  $C^{10}H^{11}N^{1}O^{8}$ , or  $C^{10}H^{12}N^{1}O^{8}$ , representing its formation by the equation :



Hesse (Ann. Ch. Pharm. cxvii. 349) suggests for this acid the formula  $C^6H^1N^2O^{10}$ . *Nitrofrangic acid* crystallises from its aqueous solution in small yellow needles; from its alcoholic solution in long, silky, orange-red needles grouped in stars. It is inodorous, has a bitterly astringent taste; detonates when heated; dissolves sparingly in cold, more abundantly and with dark crimson colour in boiling water, easily in alcohol and in ether. It is scarcely attacked by strong acids at ordinary temperatures. *Alkalis* dissolve it with violet-red colour. *Sulphydric acid* passed continuously into the aqueous solution, colours it violet-blue and forms a precipitate of sulphur; the solution then gives a violet-blue precipitate with *hydrochloric acid*.

The solution of the acid forms with the salts of the earth-metals and heavy metals precipitates which are generally of a fiery-red colour.

The *silver-salt*,  $C^{10}H^{10}AgN^3O^{17}$  crystallises in cinnabar-red needles. The *copper-salt*,  $C^{10}H^{10}CuN^3O^{17}$ , is obtained as a violet-blue precipitate, becoming violet-red when dry. Both detonate with great violence when heated.

**FRANKINCENSE.** An oleo-resin which exudes spontaneously from the spruce fir (*Abies excelsa*). According to Caillot (J. Pharm. xvi. 436), it contains 32.00 per cent. volatile oil, 7.40 resin insoluble in alcohol, 7.40 abietin, 11.47 abietic acid, and 5.57 succinic acid and extractive matter. When melted in water and strained through a cloth, it forms *Burgundy pitch*. (*Pereira's Materia Medica*, 4th ed. ii. 366.)

The substance used as incense in religious ceremonies is OLIBANUM (*q. v.*)

**FRANKLINITE.** A mineral consisting mainly of the sesquioxides of iron and manganese combined with the protoxides of zinc and iron. It occurs crystallised in forms of the regular system, chiefly the octahedron and dodecahedron, also the cube, icosi-tetrahedron 202 (*fig.* 180), and triakis-octahedron, 20 (*fig.* 183), and in combinations like *figs.* 194, 195, 196, 199, 200, 202, and others. Cleavage octahedral, indistinct. It likewise occurs massive, coarse or fine-granular to compact. Hardness = 5·5 to 6·5. Specific gravity = 5·07 to 5·09. Lustre metallic. Colour iron-black. Streak dark reddish-brown. Opaque. Fracture conchoidal. Brittle. Acts slightly on the magnet. Infusible before the blow-pipe; when strongly heated on charcoal, it yields oxide of zinc; gives the manganese reaction with borax.

From the mean of five analyses by Rammelsberg (*Mineralchemie*, p. 169), it is found to contain 25.30 ZnO, 64.51 Fe<sup>2+</sup>O, and 13.51 Mn<sup>2+</sup>O = (103.32) or 45.16 iron, 9.38 manganese, 20.30 zinc, and 25.16 oxygen (= 100), whence Rammelsberg deduces the formula  $\frac{1}{2}\text{Fe}^2\text{O} \cdot \frac{1}{2}\text{Mn}^2\text{O} \cdot \text{ZnO}$ , which is of the general form  $3\text{M}^2\text{O} \cdot \text{R}^2\text{O}^3$  or  $(\text{R}^2)^{--}\text{O}^3$ .

Franklinite was formerly regarded as belonging to the spinel group  $M_2O \cdot R_2O_3$ , with which, indeed, it agrees in crystalline form; but this formula appears to have been deduced from incorrect analyses.

Franklinite occurs abundantly at Hamburg, New Jersey, near the Franklin furnaces, together with red oxide of iron and garnet, in granular limestone; also at Stirling Hill in the same locality, where it is associated with willemite. The attempts to work it for zinc have proved unsuccessful; but it is ground up to a dark paint, and used also as an ore of iron. The mine is said to give increased tenacity to the iron. Franklinite is also said to occur in amorphous masses at Altenberg, near Aix-la-Chapelle. (Dana, ii. 106.)

**FRAXITIN.**  $C^{18}H^{20}O^4$ . (Salm-Horstmar, Pogg. Ann. *cvii.* 327.—Rochleder, *ibid.* 331.)—A compound formed, together with glucose, by digesting fraxin with dilute sulphuric acid. (See **FRAXIN**.)

It separates from the acid liquid in colourless needle-shaped crystals, or dendritic groups, and when recrystallised from alcohol, forms rectangular rhombic or six-sided tablets. It is inodorous, but has a slightly astringent taste. It dissolves in 1000 pts. of cold, and 300 pts. of boiling water, the hot concentrated solution having an acid reaction; somewhat more easily in alcohol, and to a slight extent in warm ether. It melts at the melting point of tin, without turning brown, and solidifies in the crystalline form on cooling.

Fraxetin dissolves in strong *sulphuric acid*, forming a bright yellow solution, from which, after dilution with water, it separates in the crystalline form on careful addition of ammonia. *Hydrochloric acid* likewise dissolves it without decomposition.



When thrown into *nitric acid*, it colours the liquid successively dark violet, garnet-red, rose-red and yellow; but the solution ultimately becomes colourless. The aqueous solution of fraxetin is coloured yellow by *ammonia* and *alkaline carbonates*, also by *baryta*, *strontia*, and *lime* in the solid state, the baryta and strontia becoming covered with a red and afterwards with a blackish green deposit, and the lime first with an orange-coloured, and then with a brownish deposit. The carbonates of the earth-metals colour the solution of fraxetin yellow, and give rise to the formation of a precipitate insoluble in pure water, and exhibiting a green fluorescence. The acetates of *barium* and *strontium* colour the solution yellow, and on evaporating it, a green substance remains with the crystals. Nitrate of silver added to the solution forms a black cloud; ferric chloride colours the liquid greenish-blue; carbonate of lead immersed in it, acquires a lemon-yellow colour. Fraxetin dissolves in acid sulphite of ammonium, forming a solution which is merely coloured yellow by ammonia, being thereby distinguished from *æsculetin*, the yellowish solution of which in acid sulphite of ammonium assumes a darker colour on addition of ammonia, and when subsequently shaken up with air, becomes blood-red, and finally dark indigo-blue. (Rochleder, *Gm.* xvi. 24.)

**FRAXIN.** *Paviin*.—A fluorescent substance existing in the bark of the common ash-tree (*Fraxinus excelsior*), and probably in that of other species of *Fraxinus*; also, together with *æsculin*, in the bark of the horse-chestnut (*Æsculus Hippocastanum*); and apparently of all species of the genera *Æsculus* and *Pavia*. L. Gmelin, in 1840 (*Ann. Ch. Pharm.* xxxvii. 352), first observed that a decoction of the bark of the manna ash (*Fraxinus ornus*, L.), exhibits a peculiar blue colour by reflected light, and attributed this appearance to a peculiar iridescent substance (*Schillerstoff*) existing in the bark. Salm-Horstmar in 1856 (*Pogg. Ann.* xlvii. 637) observed a similar appearance (fluorescence) in the infusion of the bark of *Fraxinus excelsior*, and in 1857 (*Pogg. Ann.* c. 607),\* he obtained the substance on which this effect depends, in the separate state, examined many of its properties, and gave it the name of fraxin. This substance was further examined and analysed by Rochleder (*Pogg. Ann.* cvii. 331). Stokes in 1858 (*Chem. Soc. Qu. J.* xi. 17) obtained from horse-chestnut bark, previously known to contain a substance exhibiting a sky-blue fluorescence, viz. *æsculin* (i. 60), another fluorescent substance exhibiting a bluish-green tint, to which he gave the name *paviin*, from the genus *Pavia*, in all species of which it appears to exist in greater abundance than in the genus *Æsculus*. Subsequently, in 1859 (*Chem. Soc. Qu. J.* xii. 126), Stokes suggested that this body, *paviin*, was identical with fraxin, and the correctness of this idea has been demonstrated by the experiments of Rochleder, who has also obtained fraxin from horse-chestnut bark.

*Preparation*.—*a.* From the bark of *Fraxinus excelsior*. The decoction of the bark stripped at the flowering time is precipitated by neutral acetate, and the filtrate by basic acetate of lead; the latter precipitate is diffused in water and decomposed by sulphydric acid; and the liquid is evaporated to the crystallising point. (Salm-Horstmar.)

*b. From Horse-chestnut bark*.—1. The aqueous decoction of the bark is mixed when cold with such a quantity of a ferric salt, that on adding ammonia to a sample of the liquid, the precipitate immediately separates in flocks, and the supernatant liquid exhibits a yellow colour and strong fluorescence; the whole is then precipitated by ammonia; about one-fourth of the filtrate precipitated by acetate of lead, avoiding an excess; the precipitate immediately redissolved by addition of acetic or of dilute nitric acid; this solution added to the remaining three-fourths of the above-mentioned filtrate after the latter has been acidulated; the mixture precipitated by ammonia (*A*), the filtrate with basic acetate of lead (*B*); the two precipitates separately dissolved in acetic acid; and the filtered solutions left to crystallise.

The solution of *A* yields fraxin (*paviin*), and that of *B*, *æsculin* (Stokes). Fraxin or *paviin* may also be separated from *æsculin* by its greater solubility in ether. (i. 60.)

2. Horse-chestnut bark is exhausted with alcohol of 35° Bm.; the filtered decoction is precipitated by an alcoholic solution of neutral acetate of lead; the precipitate (containing fraxin and the tannic acid of the bark) is washed with alcohol, suspended in water, and decomposed by sulphydric acid; the fluorescent watery liquid is evaporated in vacuo over oil of vitriol; the pulverised residue is treated with a small quantity of water at 0° C.; the tannic acid solution is rapidly separated from the crystals of fraxin; and the crystals are purified by recrystallisation. (Rochleder.)

*Properties*.—Fraxin crystallises in tufts of yellowish-white needles (Salm-Horstmar); in colourless crystals resembling those of sulphate of zinc (Rochleder). It

\* Keller, in 1853 (*Repert. Pharm.* xlv. 438), by precipitating the aqueous decoction of ash-bark with basic acetate of lead, and evaporating the filtrate, obtained bitter prisms, regarded by him as a base, and designated by Buchner as *fraxinine*. Rochleder and Schwarz (*Ann. Ch. Pharm.* lxxxvii. 186), by the same process, obtained a bitter brownish-yellow extract containing needle-shaped crystals, which, when purified, proved to be nothing but mannite, a result corroborated by Stenhouse (*Phil. Mag.* [4], vii. 501).

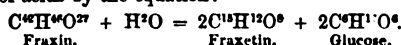


is inodorous, but has a slightly bitter and afterwards astringent taste. It dissolves sparingly in cold, easily in hot water, sparingly in cold, moderately in hot alcohol; and is separated from the alcoholic solution by animal charcoal; insoluble in ether (Salm-Horstmar), more soluble in ether than æsculin (Stokes).<sup>\*</sup> The concentrated aqueous solution is yellow and has an acid reaction; when largely diluted, it exhibits by daylight a strong blue fluorescence (blue-green according to Stokes, who moreover, finds that the optical properties of fraxin from ash-bark, and of pavin from horse-chestnut bark, are absolutely identical). The fluorescence is increased by the presence of a trace of alkali, but disappears on addition of acids. The alcoholic solution is likewise fluorescent (Salm-Horstmar).

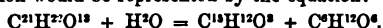
The aqueous solution is coloured sulphur-yellow by alkalis, the crystals also turning yellow in air containing ammonia; it is coloured green by ferric chloride, and then yields a lemon-yellow precipitate; it likewise forms a yellow precipitate with acetate of lead. (Salm-Horstmar.)

Fraxin (from ash-bark) melts at a gentle heat (Salm-Horstmar), at 320° C. forming a red liquid (Rochleder) and solidifies to an amorphous mass, which, according to Rochleder, dissolves in water with orange-red colour. At a higher temperature, it decomposes, yielding a crystalline sublimate, soluble in water, and forming a solution which becomes yellow and fluorescent on addition of ammonia.

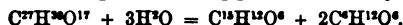
Fraxin digested with dilute sulphuric acid is resolved into glucose and fraxetin. The equation which represents this decomposition, varies of course, according to the formula assigned to fraxin, which cannot be considered as definitively settled. Rochleder, from his first analyses of fraxin (from ash-bark) dried between 100° and 120°, assigned to it the formula  $C^{22}H^{22}O^{17}$  or  $C^{22}H^{22}O^{17}$ , and represented its decomposition under the influence of acids by the equation:



Wurtz, however (Rép. Chim. pure, i. 473), concluded from Rochleder's own analyses, that its formula was most probably  $C^{22}H^{22}O^{23}$  or  $C^{22}H^{22}O^{19}$ , according to which its decomposition would be represented by the equation:



More recently, Rochleder (Pogg. Ann. cvii. 331) from the quantity of glucose yielded by the decomposition of fraxin (from horse-chestnut bark) concludes that its formula is  $C^{22}H^{22}O^{17}$ , its decomposition taking place as shown by the equation:



**FRAXINITE.** See foot-note, p. 708.

**FRAXINITE.** A name applied by Mouchon (Vierteljahrs. per Pharm. iii. 433) to the dried extract of ash-leaves, previously precipitated by basic acetate of lead and freed from excess of lead by sulphydric acid. It is not a definite substance.

**FRAXINUS.** The dried leaves of the common ash (*Fraxinus excelsior*) contain, according to Sprengel (J. f. ökonom. Chem. vii. 269) 39.3 per cent. of substances soluble in water (tannin, &c.), 42.3 per cent. matter soluble in dilute potash, also wax, resin, woody-fibre, &c. and 6.22 per cent. ash. According to Garot (J. Pharm. [3] xxiv. 308) the leaves contain a large quantity of malate of calcium.

The soft white wood of the same tree, of specific gravity 0.7 to 0.9, yields 2.3 per cent. ash (Mollerat), 0.55 (Sprengel).

The following is the composition of the ash of the wood and leaves, according to Sprengel's analysis.

	K <sup>2</sup> O	Na <sup>2</sup> O	Ca <sup>2</sup> O	Mg <sup>2</sup> O	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	Mn <sup>2</sup> O <sup>3</sup>	SO <sup>3</sup>	P <sup>2</sup> O <sup>5</sup>	SiO <sup>2</sup>	Cl
Leaves .	22.2	2.6	50.3	6.3	0.02			5.1	6.6	2.3	2.9 = 99.3
Wood .	22.0	24.3	23.1	5.8	2.3		1.6	3.1	1.5	2.3	2.0 = 100.0

The existence of a fluorescent substance, fraxin, in ash bark has been noticed in a preceding article. The aqueous decoction of the bark exhibits the blue or blue-green fluorescence due to fraxin; the alcoholic extract exhibits a blood-red fluorescence from admixture of chlorophyll with the fraxin. (Salm-Horstmar.)

The seed of the ash tree, formerly used officinally, as *Semen lingua avis*, yields to ether 16 per cent. of an oil having the odour of bugs. (Keller, Buchn. Repert. xlv. 439.)

The bark of the manna ash (*Fraxinus ornus*, L.; *Ornus europæus*, Pers.) contains manna, which exudes from it, partly spontaneously, but more freely from incisions. The same bark contains a fluorescent substance (L. Gmelin, p. 708), probably fraxin,

<sup>\*</sup> This observation applies to fraxin from ash-bark, as well as to pavin from horse-chestnut bark. (Chem. Soc. Qu. J. xli. 17.)

and according to Dufour (Compt. rend. li. 31), easily yields a fluorescent aqueous infusion.

**FREIBERGITE.** An argentiferous variety of tetrahedrite. (Dana, ii. 512.)

**FREISLEBENITE.** *Antimonial Sulphuret of Silver.* *Schilfglaserz.*—A mineral occurring in monoclinic prisms longitudinally striated and cleaving parallel to  $\infty P$ . Hardness = 2–2.5. Specific gravity 6.4–6.194 (Hausmann). Lustre metallic. Colour and streak light steel-grey, inclining to silver-white; also blackish lead-grey. Yields easily to the knife and is rather brittle. Fracture conchoidal to uneven. Before the blowpipe on charcoal, it emits copious white vapours and a slight sulphurous odour, deposits oxide of antimony and oxide of lead round the assay, and finally leaves a white metallic globule.

*Analyses.*—1. From the Himmelsfürst mine near Freiberg. Specific gravity 6.194 (Wöhler, Pogg. Ann. xlv. 146).—2. From Hiendelencina in Spain. Specific gravity 5.6–5.7 (Escosura, Ann. Min. [5] viii. 495).—3. From Příbram, Bohemia (Payr, Jahresber. d. Chem. 1860, p. 746).

	S	Sb	Pb	Ag	Cu	Fe	
1.	18.74	27.38	30.27	22.93	1.22	0.11	= 100.65
2.	17.60	26.83	31.90	22.45	.	.	= 98.78
3.	18.41	27.11	30.77	23.08	.	0.68	= 100.05

From the second analysis, Rammelsberg (*Mineralchemie*, p. 82) deduces the formula  $9M^2S_4Sb^2S^3$  which may be supposed to be made up of  $3(2M^2S.Sb^2S^3) + 3M^2S.Sb^2S^3$ , or  $3M^2Sb^2S^3.2M^2Sb^2S^3$ , the first member of which is analogous to Brogniardite and Jamesonite, the second to red silver ore and Boulangerite.

Freislebenite occurs also at Kapnik in Transylvania and at Ratiborwitz, the ore of this last region containing bismuth, according to Zincken. An antimonial sulphide of silver is said to occur with native silver and native copper at the copper mines of Michigan. (Dana, ii. 79).

**FRENCH BERRIES.** See YELLOW BERRIES; also RHAMNUS.

**FRENCH POLISH.** A solution of shellac in alcohol, sometimes also containing gum elemi and copal. (See *Ure's Dictionary of Arts, &c.*, ii. 298.)

**FRITILLARIA IMPERIALIS.** *Crown Imperial.*—The bulbs of this plant are recommended by Basset (Compt. rend. xxxvii. 408) as a substitute for the potato, especially as a source of starch, of which they contain a rather larger proportion than the potato, as will be seen by the following table.

	Water.	Starch.	Soluble matter.	Dry residue.
Potato . . . . .	70 . . . . .	20 . . . . .	4 . . . . .	6 . . . . .
Crown Imperial . . . . .	68 . . . . .	23 . . . . .	5 . . . . .	4 . . . . .

**FRITT.** A term applied to the mixture of the materials for glass-making, after it has been calcined at a heat not sufficient to melt it.

**FRUIT.** The word fruit, in botanical language, signifies the ovary or seed-vessel arrived at maturity, or in its progress towards maturity after the impregnation of the seed. Every fruit consists of two parts, the seed and the pericarp, the latter comprising everything that is external to the seed, and being formed of the integuments of the ovary, often greatly thickened and hardened, together with any parts of the flower, such as bracts, calyxes, &c. that may remain attached to the ovary after impregnation. The pericarp, moreover, consists of three parts, the epicarp, which is the external integument or skin, the endocarp or putamen, which is the inner coat or shell, and the sarcocarp or mesocarp, intermediate between the other two, and generally having a more or less fleshy consistence; it is, in fact, the sarcocarp which forms the fleshy or pulpy mass of those succulent fruits, such as the apple, pear, peach, plum, grape, &c., to which the term fruit is mostly applied in ordinary language.

All parts of the flower are modifications of the leaf, the ovary in particular being made up of a leaf or a number of leaves folded or rolled up. Hence it may be expected that the fruit in its early stages of development, will have much the same chemical composition as the leaves themselves, and will be acted upon in the same manner by external agencies. Unripe fruits are, in fact, almost always green, and, like other green parts of the plant, decompose the carbonic acid of the air, liberating the oxygen and assimilating the carbon, and forming within their cells a variety of compounds, some soluble in water, such as vegetable acids, gum, and sugar, others insoluble, such as cellulose, pectose, and starch; at the same time they take up a certain amount of inorganic salts. During the whole of this stage, the fruit increases rapidly in bulk and weight. But as it approaches maturity, it loses its green colour, becoming brown, yellow, or red, and then no longer acts on the air like the leaves, but on the contrary absorbs oxygen, which unites with a portion of the carbon and hydrogen of the fruit, converting them into carbonic acid and water, which are given off. In this latter stage, indeed, the fruit undergoes a slow combustion, several of the proximate principles which it contains in the unripe state, chiefly the vegetable acids and tannin, being

thereby burnt away, so that the fruit becomes less sour and astringent; at the same time, the starch in the cells of the fruit is transformed into sugar, and the insoluble pectose into pectin and other soluble substances of allied composition, and having more or less of a gelatinous character. It is in this state that the fruit is generally eaten; if left for a longer time on the tree, and in many cases by mere exposure to the air after removal, it undergoes a further oxidation, by which the sugar and the remaining acid are likewise destroyed, so that the fruit becomes insipid; in this state it is said to be over-ripe. After a still longer time, the cellulose itself is attacked, so that the pericarp is ultimately destroyed and the seed set at liberty.

The diminution of acidity in fruits as they ripen, is sometimes attributed to neutralisation of the free acids by alkalis conveyed to the fruit by the sap; the sour taste is also said to be masked by the sugar and gelatinous substances developed in the course of maturation. The latter explanation is doubtless true to a certain extent, but with regard to the former, direct experiments by Decaisne and Frémy have shown that the proportion of mineral bases does not increase as the fruit ripens, but that, on the other hand, the proportion of acid in the ripe fruit is always less than in unripe, the decrease, as already observed, being due to oxidation. (Pelouze et Frémy, *Traité*, iv. 361.)

The following analyses by Bérard (*Gmelin's Handbuch*, viii. [1] 154) of fruits in the ripe and unripe state — which must be regarded as merely approximate — confirm in a general way the view of the ripening process above given, showing that, as the fruit ripens, the sugar increases, the gum sometimes increases, sometimes decreases, the woody fibre increases to a certain extent absolutely, but diminishes relatively to the weight of the entire fruit. With regard to the relative quantity of acid in the ripe fruit, Bérard's analyses show an increase in most cases, which is contrary to the results obtained by Frémy; the latter are doubtless the more trustworthy of the two.

*Composition of ripe and unripe Fruit. (Bérard.)*

	Summer Peaches.		Greengages.		Apricots.		
	unripe.	ripe.	unripe.	ripe.	unripe.	somewhat riper.	ripe.
Chlorophyll . . . . .	0.27	0.0	0.03	0.08	0.04	0.03	
Yellow colouring matter . . . . .							0.10
Sugar . . . . .	0.63	11.61	17.71	24.81	trace	6.64	16.48
Gum . . . . .	4.22	4.85	6.53	2.06	4.10	4.47	5.12
Woody fibre . . . . .	3.01	1.21	1.26	1.11	3.61	2.53	1.86
Nitrogenous matter . . . . .	0.41	0.93	0.45	0.28	0.76	0.34	0.17
Malic acid . . . . .	1.07	1.10	0.45	0.56	2.70	2.30	1.80
Lime . . . . .	0.08	0.06	trace	trace	very small quantities		
Water . . . . .	90.31	80.24	74.57	71.10	89.39	84.49	74.87
	100.00	100.00	100.00	100.00	100.00	100.80	100.40

100 pts. of unripe summer peaches were estimated to yield 179 pts. ripe fruit.

100 pts. of unripe greengages were estimated to yield 129 pts. ripe fruit.

100 pts. of unripe apricots were estimated to yield 200 pts. ripe fruit.

	Gooseberries.		Cherries.		Pears.		
	unripe.	ripe.	unripe.	ripe.	hard.	soft.	over-ripe.
Chlorophyll . . . . .	0.03		0.05		0.08	0.01	0.04
Red colouring matter . . . . .			not exactly determined.				
Sugar . . . . .	0.52	6.24	1.12	18.12	6.45	11.82	8.77
Gum . . . . .	1.36	0.78	6.01	3.23	3.17	2.97	2.62
Woody fibre . . . . .	8.45	8.01	2.44	1.12	3.80	2.19	1.85
Nitrogenous matter . . . . .	1.07	0.86	0.21	0.57	0.08	0.21	0.23
Malic acid . . . . .	1.80	2.41	1.75	2.01	0.11	0.08	0.61
Citric acid . . . . .	0.12	0.31					
Lime . . . . .	0.24	0.29	0.14	0.10	0.03	0.04	trace
Water . . . . .	86.41	81.10	88.28	74.55	86.28	83.88	62.73
	100.00	100.00	100.00	100.00	100.00	100.00	76.85

In the gooseberries, the seeds as well as the pulpy matter are included in the woody fibre. The hard pear was ripe, and analysed immediately after it was plucked; the



soft pear was of the same variety, and had been kept for some time exposed to the air, the oxygen of which it had converted, without change of volume, into carbonic acid, losing at the same time 0.77 per cent. carbon and becoming richer in sugar and poorer in gum and woody fibre. The over-ripe pear, also of the same variety, had been kept till its weight was reduced from 100 to 76.85 parts.

A very important part of the ripening process in succulent fruits, such as the apple, pear, plum, grape, &c., those in short to which the term fruit is applied in ordinary language, consists in the gradual transformation of substances of the pectous group.

Unripe fruits contain pectose, a substance insoluble in water, alcohol, and ether; which, by the action of the acids in the fruit, and of a peculiar ferment called pectase, is gradually transformed into other substances, pectin, pectic acid, pectosic acid, &c., all soluble in water, possessing more or less of a gelatinous character, and differing in composition from pectose only by containing one or more molecules of water in addition. The first change appears to consist in the conversion of the pectose into pectin and parapectin by the action of the acids (chiefly citric and malic) of the fruit under the influence of heat, the fruit at the same time losing its hardness. As the process of ripening advances, the pectin and parapectin likewise disappear, being converted successively, by the action of pectase, into pectosic, pectic, and metapectic acids. Over-ripe fruits always contain metapectic acid, without a trace of pectin.

The conversion of the starch of the unripe into the sugar of the ripe fruit is effected partly by the citric and malic acids, partly by the metapectic acid.

When fruits are boiled, the formation of pectin takes place in the same manner as in the ripening, the action being likewise accelerated by the presence of acids. The formation of jelly, which takes place after some time, depends upon the conversion of pectin, by the action of pectase, into pectic or pectosic acid, or on the solution of the pectic acid in the salts of an organic acid contained in the fruit. The juice of gooseberries often gelatinises very quickly when mixed with that of raspberries; because the latter is rich in pectase, which converts the pectin of the former into gelatinous pectosic acid. (Frémy, *Ann. Ch. Phys.* [3] xxiv. 5; *Jahresber. d. Chem.* 1847-8, p. 807.)

According to Buignet (*Ann. Ch. Phys.* [3] lxi. 230), the sugar of fruits is formed, not from starch, but from an astringent substance resembling tannin, which is contained in the unripe fruit, and diminishes in quantity as the fruit ripens. This substance is said by Buignet to unite with iodine even more readily than starch, forming a colourless insoluble compound, which is converted by dilute acids into dextroglucose, identical with that formed from starch. Buignet further states, that the presence of starch cannot be detected in any green fruit, excepting the banana, either by iodine or by the microscope.

Payen, on the other hand (*Compt. rend.* liii. 313), has given a method by which the presence of starch in unripe fruits and its gradual conversion into sugar may be easily demonstrated. A thin slice cut out of the middle of the fruit is washed with water, and immersed in an aqueous solution of iodine mixed with a little alcohol; a blue colour is then immediately produced, varying in intensity according to the quantity of starch present. The reaction is, however, often masked by the presence of coloured or colouring matters, or of nitrogenous compounds in the fruit; moreover, the starch, when present in very small and only partially united granules, quickly loses the colour produced by iodine.

These or similar causes of error may perhaps have led to the negative results obtained by Buignet as to the presence of starch in unripe fruits.

The sugar of fruits consists partly of cane-sugar,  $C^{12}H^{22}O^{11}$ , partly of inverted sugar,  $C^{12}H^{24}O^{12}$ , a *laevo*-rotatory uncrystallisable sugar, identical in composition and optical rotatory power with the mixture of *laevo*- and *dextro*-glucose produced from cane-sugar by the action of acids, or of Berthelot's glucose-ferment (*q.v.*). According to Buignet (*loc. cit.*), the cane-sugar is formed first, and is gradually but in most cases only partially transformed, during maturation, into inverted sugar, the changes being produced, not by the action of acids (for the quantity of inverted sugar in different fruits bears no proportion to the quantity of acid present), but to a nitrogenous substance resembling Berthelot's glucose-ferment obtained from yeast. This statement respecting the conversion of the cane-sugar into inverted sugar is, however, not quite in accordance with the observations of Berthelot and Buignet (*Compt. rend.* li. 1094) on the formation of sugar during the ripening of oranges; from which it appears that the inverted sugar predominates in the unripe, and the cane-sugar in the ripe fruit, and that the weight of the inverted sugar alters but little, whereas that of the cane-sugar increases during ripening in proportion to the weight of the entire fruit, as well as to that of the juice and of the solid substances contained in it.

The following table contains the analyses of a considerable number of ripe fruits by Fresenius, and others working under his direction (*Ann. Ch. Pharm.* ci. 219; *Jahresber. d. Chem.* 1857, 635). The fruit having been pressed or saturated, and the soluble and

COMPOSITION OF EDIBLE FRUITS.

	Gooseberries.						Currants.				Strawberries.		Raspberries.					
	Large red.	Small red.		Middle-sized yellow.		Large smooth red.	Middle-sized red.		Very large red.	Middle-sized white.		Wild.	Light red pine; quite ripe.	Wild red.	Cultivated white.			
Sugar . . . . .	8.063	6.030	8.239	6.383	7.507	6.483	4.78	6.44	5.647	6.61	7.692	7.12	3.247	4.550	7.575	3.597	4.708	3.703
Free acid . . . . .	1.368	1.573	1.589	1.078	1.334	1.6.64	2.31	1.84	1.696	2.26	2.268	2.53	1.650	1.332	1.133	1.980	1.366	1.115
Aluminous substances . . . . .	{ 0.441	0.445	0.358	0.578	0.369	0.306	0.46	0.49	0.356	0.77	{ 0.300	{ 0.68	0.619	0.567	0.359	0.546	0.544	0.655
Pectous substances, &c. . . . .	{ 0.969	0.513	0.522	2.112	2.113	0.843	0.28	0.19	0.007	0.18	{ 0.19	{ 0.19	0.145	0.049	0.119	1.107	1.746	1.397
Ash . . . . .	0.317	0.452	0.504	0.200	0.277	0.553	0.54	0.57	0.620	0.54	0.560	0.70	0.737	0.603	0.480	0.270	0.481	0.380
Soluble matter . . . . .	11.148	9.013	11.312	10.351	11.600	9.849	8.36	9.53	8.385	10.36	10.810	11.33	8.398	7.101	9.686	7.500	8.835	7.260
Seeds . . . . .	2.481	{ 2.442	2.629	{ 3.380	2.081	2.803	{ 4.45	4.48	3.940	4.94	4.144	4.85	6.032	5.580	1.960	8.460	4.106	4.520
Skins, &c. . . . .	0.512						0.66											
Pectose . . . . .	0.294	0.515	1.428	0.308	0.955	0.390	0.69	0.72	2.380	0.53	0.240	0.51	0.299	0.300	0.900	0.180	0.502	0.040
Ash . . . . .	{ 0.146	{ 0.069	{ 0.247	{ 0.100	{ 0.170	{ 0.133	{ 0.11	{ 0.23	{ 0.185	{ 0.12	. . .	{ 0.14	{ 0.315	{ 0.345	{ 0.154	{ 0.134	{ 0.296	{ 0.081
Insoluble matter . . . . .	3.287	2.957	3.957	4.130	3.036	3.183	5.80	5.20	6.390	5.47	4.394	5.36	6.331	5.880	2.860	8.040	4.608	4.560
Water . . . . .	85.565	83.030	84.831	85.519	85.364	86.958	85.84	85.27	85.355	84.17	84.806	83.42	87.271	87.019	87.474	83.860	86.557	88.180





COMPOSITION OF EDIBLE FRUITS—continued.

	Musc. Plums.		Apricots.			Peaches.		Apples.					Pears.	
	Common	Italian, very sweet.	Fine, rather large.	Large fine-flavoured.	Small.	Large Dutch.	Similar variety.	Large English reamets.	White dessert apple.	Borndorff apple.	White mealy apple.	English winter golden pippin.	Sweet red.	
Sugar . . .	5.793	6.730	1.140	1.531	2.736	1.580	1.565	9.25	5.96	6.83	7.61	10.36	7.940	
Free acid . .	0.952	0.841	0.898	0.766	1.603	0.612	0.734	0.53	0.39	0.85	0.61	0.48	traces	
Albuminous substances . .	0.785	0.832	0.832	0.389	0.411	0.463	11.058	0.52	0.45	0.22	6.85	5.11	0.260	
Pectones . .	3.646	4.105	5.929	9.283	5.562	6.313		1.80	6.47	2.72			3.35	0.281
Starches, &c. .	0.734	0.590	0.820	0.754	0.723	0.422	0.913	0.22	0.36	0.44	0.285	0.284		
Ash . . .														
Soluble matter .	11.910	13.098	9.619	12.723	11.035	9.390	14.270	11.56	14.70	14.96	15.07	15.95	19.870	
Seeds . . .	3.540	3.124	4.300	3.216	3.415	4.629	6.764	0.07	0.38	0.38	0.390	0.390	3.518	
Skins, &c. .	1.990	0.972	0.967	0.944	1.248	0.991	2.420	1.71	1.42	1.42	0.390	0.390	3.420	
Pectose . .	0.630	1.534	0.148	1.002	0.780		(0.042)	(0.163)	1.49	1.16	1.16	1.340	1.340	0.805
Ash . . .	(0.094)	(0.066)	(0.071)	(0.104)	(0.060)			0.06	(0.03)	(0.03)	0.050	0.050	(0.049)	
Insoluble matter	6.160	5.680	5.415	5.162	5.413	5.680	9.164	2.39	3.27	3.00	2.44	2.18	4.123	
Water . . .	81.930	81.272	84.966	82.115	83.552	84.960	76.546	86.03	82.03	82.04	82.49	82.13	83.950	
													83.007	

insoluble portions separated by straining through a colander, determinations were made in separate portions of the former; of the amount of dry substance, ash, sugar (by means of Fehling's solution of cupric oxide and soda), free acid (by titration with caustic soda), and albuminous substances (by determining the amount of nitrogen, and reckoning 100 pts. of albuminous substances for every 15.5 nitrogen). The insoluble portion was dried at 100° C., and the amount of ash determined; when possible, the weight of the stones or kernels was separately estimated; and a separate portion of the insoluble matter was digested for some time with dilute sulphuric acid, to determine the amount of pectous substances left undissolved by that acid.

The *sugar* in the table consists of glucose and fruit-sugar (dextro- and levo-glucose); the amount of *free acid* is reduced to its equivalent in malic acid; *pectous substances*, &c., denotes soluble substances of the pectous group, together with gum, colouring matter, suspended fat, and combined organic acids. The *ash* of the insoluble portion is already included in the weight of the kernels, skins, &c., and is therefore placed within brackets.

From these analyses, the following comparative estimates may be made of the average amount of sugar, free acids, pectin, &c., in different kinds of fruit.

#### I. Comparison of Fruits as to their average Amount of Sugar.

	Per cent.		Per cent.
Peach . . . . .	1.57	Currant . . . . .	6.10
Apricot . . . . .	1.80	Mussel Plum . . . . .	6.26
Plum, round red . . . . .	2.12	Gooseberry . . . . .	7.15
Greengage . . . . .	3.12	Red Pear . . . . .	7.45
Mirabelle . . . . .	3.58	Apple . . . . .	8.37
Raspberry . . . . .	4.00	Sour Cherry . . . . .	8.77
Blackberry . . . . .	4.44	Mulberry . . . . .	9.19
Strawberry . . . . .	5.73	Sweet Cherry . . . . .	10.79
Bilberry . . . . .	5.78	Grape . . . . .	14.93

#### II. Comparison of Fruits as to their average Amount of free Acid, reduced to its Equivalent in Malic acid.

	Per cent.		Per cent.
Red Pear . . . . .	0.07	Blackberry . . . . .	1.19
Mirabelle . . . . .	0.58	Sour Cherry . . . . .	1.28
Sweet Cherry . . . . .	0.62	Plum, round red . . . . .	1.30
Peach . . . . .	0.67	Strawberry . . . . .	1.31
Grape . . . . .	0.74	Bilberry . . . . .	1.34
Apple . . . . .	0.75	Gooseberry . . . . .	1.45
Mussel Plum . . . . .	0.89	Raspberry . . . . .	1.48
Greengage . . . . .	0.91	Mulberry . . . . .	1.86
Apricot . . . . .	1.09	Currant . . . . .	2.04

#### III. Comparison of Fruits as to their average Proportion of Acid, Sugar, Pectin, Gum, &c.

	Acid.	Sugar.	Pectin, Gum, &c.		Acid.	Sugar.	Pectin, Gum, &c.
Plum, round red . . . . .	1	1.63	3.14	Gooseberry . . . . .	1	4.93	0.76
Apricot . . . . .	1	1.65	6.35	Mulberry . . . . .	1	4.94	1.10
Peach . . . . .	1	2.34	11.94	Mirabelle . . . . .	1	6.20	9.92
Raspberry . . . . .	1	2.70	0.96	Sour Cherry . . . . .	1	6.85	1.43
Currant . . . . .	1	3.00	0.07	Mussel Plum . . . . .	1	7.03	4.35
Greengage . . . . .	1	3.43	11.83	Apple . . . . .	1	11.16	5.60
Blackberry . . . . .	1	3.73	1.21	Sweet Cherry . . . . .	1	17.29	2.76
Bilberry . . . . .	1	4.31	0.41	Grape . . . . .	1	20.18	2.03
Strawberry . . . . .	1	4.37	0.08	Red Pear . . . . .	1	94.60	44.40

#### IV. Comparison of Fruits as to their average Proportion of Water, and of Soluble and Insoluble Constituents.

	Water.	Soluble.	Insoluble.		Water.	Soluble.	Insoluble.
Raspberry . . . . .	100	9.12	6.88	Red Pear . . . . .	100	14.25	5.54
Blackberry . . . . .	100	9.26	6.46	Peach . . . . .	100	14.64	2.10
Strawberry . . . . .	100	9.39	5.15	Mussel Plum . . . . .	100	15.32	3.15
Plum, round red . . . . .	100	9.74	0.87	Sour Cherry . . . . .	100	16.48	1.31
Currant . . . . .	100	11.00	6.62	Mulberry . . . . .	100	16.57	1.47
Bilberry . . . . .	100	12.05	16.91	Apple . . . . .	100	16.89	3.61
Gooseberry . . . . .	100	12.18	3.57	Greengage . . . . .	100	18.52	1.22
Mirabelle . . . . .	100	13.04	1.53	Sweet Cherry . . . . .	100	18.61	1.53
Apricot . . . . .	100	13.31	2.07	Grape . . . . .	100	22.81	5.81

The very small amount of albuminous substance in fruits (see Table, pp. 713-715) shows that they cannot be regarded as nutritious articles of diet; in fact, an egg weighing 45 grms., and containing 5 grms. of albuminous matter, is equivalent in nutritive power to 550 grms. of cherries, 690 grms. grapes, 970 grms. strawberries, 1260 grms. apples, and 2000 grms. (or 4 lbs.) of red pears. The great excess of non-azotised matter in fruits shows that they possess rather the character of so-called respiratory food. In this respect a pound of starch, or about 5.5 lbs. of potatoes, might be replaced by 5.4 lbs. grapes, 6.5 lbs. greengages, 6.7 lbs. cherries, 6.7 lbs. apples, 7.8 lbs. red pears, 7.8 lbs. mussel plums, 9.4 lbs. gooseberries, 10.8 lbs. currants, 12.3 lbs. strawberries, and 12.9 lbs. raspberries.

The value of fruit as an article of diet depends, however, chiefly on its refreshing character and agreeable taste, on the demulcent qualities of the gum and pectin, and on the physiological action of the free acid and alkaline salts contained in it. The efficacy of lemon-juice as a remedy for sea-scurvy, may be attributed in a great degree to the large quantity of potash-salts which it contains, inasmuch as the deficiency of potash in the salt-meat, which forms so large a proportion of the diet of sea-faring men, appears to be one of the chief causes of that disease.

The agreeable taste of fruit depends partly on its aroma, partly on a due proportion between the acid, sugar, gum, pectin, &c., and between the water, the soluble, and the insoluble constituents. Luscious fruits, like the peach, greengage, and mulberry, which seem to melt in the mouth, contain a very large proportion of soluble substances. A due proportion of gum, pectin, and other gelatinous substances serves to mask the taste of the free acid, if present in rather large proportion as compared with the sugar. Such is the case with the peach, apricot, and greengage (Table III., p. 716), which contain but a small quantity of sugar as compared with the free acid, but a large proportion of gum and pectous substances.

The very sour taste of certain baccate fruits, as the currant and gooseberry, arises from the presence of a considerable quantity of free acid, with only a small quantity of gum and pectin to disguise it.

The proportion of sugar in fruits is largely increased by cultivation, as may be seen by comparing the composition of the wild and cultivated strawberries and raspberries in the table on p. 713. (Fresenius.)

**FUCUS.** See SEA-WEED.

**FUCUSAMIDE.**  $C^4H^{12}N^2O^3$ .—A compound isomeric with furfuramide, and obtained from fucosol in the same manner as furfuramide from furfurol, namely by the action of ammonia; but as fucosol is much less soluble in ammonia than furfurol, a larger quantity of ammonia must be used in the preparation, and the two liquids mixed by frequent agitation. Fucusamide crystallises from hot alcohol in groups of long needles; its reactions are similar to those of furfuramide. (Stenhouse, Ann. Ch. Pharm. lxxiv. 289.)

**FUCUSINE.**  $C^4H^{12}N^2O^3$ . (Stenhouse, *loc. cit.*)—An organic base, isomeric with fucusamide, and therefore with furfuramide and furfurine, and obtained from fucusamide in the same manner as furfurine from furfuramide. When pure fucusamide is boiled for twenty minutes, with moderately concentrated potash or soda-ley, it melts, and is converted, without evolution of ammonia, into a slightly brown oil, which solidifies on cooling in the form of a yellowish resin. This substance contains fucusine, but does not yield that base in the crystalline form, even by solution in alcohol or ether. The best mode of obtaining the fucusine from it is to digest the mass, at a temperature a little above its melting point, with nitric acid; cool the liquid till the resin solidifies; decant the solution, and leave it to itself till the nitrate of fucusine crystallises out; purify this salt by recrystallisation from water; and decompose its pure aqueous solution with a slight excess of ammonia. The fucusine then slowly separates in small laminae united in stellate groups. This form of crystallisation distinguishes fucusine from furfurine.

*Hydrochlorate of Fucusine* is very soluble, and separates from highly concentrated solutions in short flexible needles.

*Chloroplatinate*,  $C^4H^{12}N^2O^3.HCl.PtCl^2$ .—When dichloride of platinum is added to a cold aqueous solution of hydrochlorate of fucusine, the double salt separates in the form of a yellow crystalline precipitate; but if the solutions are mixed hot, and especially if a little alcohol is added, broad four-sided prisms are obtained, having two wide and two narrow faces, and differing altogether from the long needle-shaped crystals of the corresponding furfurine-salt.

*Nitrate of Fucusine*,  $C^4H^{12}N^2O^3.NO^3H$ , crystallises from a hot aqueous solution in long prismatic needles united in stellate groups, but when crystallised from alcohol, it forms large rhombic prisms of great regularity and peculiar lustre. The crystals obtained from strong alcohol become opaque after a while, but those which separate



from a weak alcoholic solution retain their transparency. The salt when heated to  $100^{\circ}\text{C}$ . quickly becomes coloured, and decomposes.

**Oxalates of Fucusine.**—When crude fucusine is digested with excess of oxalic acid, and the solution filtered hot, the acid oxalate,  $\text{C}^9\text{H}^{12}\text{N}^2\text{O}^3\cdot\text{C}^2\text{H}^2\text{O}^4$ , is deposited in small needle-shaped crystals, which are generally coloured at first, but by repeated crystallisation and the use of animal charcoal, may be obtained in colourless silky needles. It is not very soluble in cold water, but dissolves readily in boiling water and in alcohol. The solutions have a distinct acid reaction.

The neutral oxalate resembles the acid salt in appearance, but is much more soluble.

**FUCUSOL.**  $\text{C}^9\text{H}^{10}\text{O}^2$ . (Stenhouse, Phil. Mag. [3] xviii. 122; xxxvii. 226; Ann. Ch. Pharm. xxxv. 301; lxxiv. 278.)—A volatile oil isomeric with furfural, and obtained by treating sea-weed, e. g. *Fucus nudosus*, *F. vesiculatus*, *F. serratus*, &c. with dilute sulphuric acid in the same manner as bran is treated for the preparation of furfural.

The oil thus obtained contains a large quantity of acetone, which may be removed by washing with water, redistilling at a lower temperature, and rejecting the first portion which passes over. It also contains metafurfural, or a similar impurity, from which it may be separated by repeated rectification with water, as in the purification of furfural. Lastly, it is dried over chloride of calcium and redistilled. The quantity of fucosol thus obtained from sea-weed, is only about a fourth of that of the furfural obtained from bran.

Fucosol resembles furfural in most of its properties. When recently prepared it is colourless, but turns yellow and brown in a few days, especially when it contains metafurfural. In the pure state it may be kept unaltered for a long time in hermetically sealed tubes. Specific gravity 1.150. Boiling point between  $171^{\circ}$  and  $172^{\circ}\text{C}$ . It dissolves in 14 pts. of water at  $13^{\circ}\text{C}$ . and in 12 pts. of strong aqueous ammonia at  $13.5^{\circ}$ .

Fucosol is much less stable than furfural. Sulphuric acid colours it yellowish-brown, hydrochloric acid green, and nitric acid light yellow; if, however, it contains metafurfural, all these acids colour it purple-red. Potash-ley colours it yellow at first, but the colour afterwards changes to dark-red. It imparts a deep yellow colour to the skin, and on moistening the yellow spots with aniline, a rose colour is produced (the same reaction is exhibited by furfural). With ammonia, fucosol forms fucosamide, and with sulphide of ammonium it forms thiofucosol, isomeric with thiofurfural.

Moss (*Sphagnum*) and various species of lichen (*Cetraria islandica*, *Usnea*, *Ramalina*, &c.), distilled as above with dilute sulphuric acid, yielded an oil which appeared to be identical with fucosol, inasmuch as it formed with ammonia an amide which, when treated with boiling potash-ley, formed a difficultly crystallisable base whose platinum-salt crystallised in the same form as that of fucusine (p. 717). Fern (*Pteris aquilina*) yielded an oil which appeared to be intermediate in its properties between furfural and fucosol, the base formed by treating its amide with potash, crystallising with facility and in the same form as furfuraline, while the platinum-salt resembled that of fucusine. (Stenhouse.)

**FUEL.** *Combustible; Brennstoff.*—Although this term might be correctly applied to any substance capable of combustion, its application is generally limited to those materials which are practically employed for generating heat.

The artificial application of heat for various useful purposes appears to have been always a prominent feature of distinction between man and the brute creation. In remote ages the use of fuel was, for the most part restricted to the warming of dwellings, and the preparation of food. Its industrial applications seem to have been few. In later times, however, the importance of the application of heat in the useful arts has been continually increasing. Not only is heat, generated by the combustion of fuel, the principal agent in the extraction of metals from their ores, in their subsequent fashioning into useful forms, in the manufacture of bricks, pottery, and glass, and in the various chemical arts; but, since the invention of the steam engine, it has become the most important source of motive power, in its applications both to the industrial arts and to commercial intercourse.

With this widely extended range of utility in the application of fuel, it naturally follows that the chemical principles involved in its use are of much importance. The general nature of the phenomena of combustion and the development of heat being described under the heads COMBUSTION and HEAT, it will only be requisite here to show in what manner the value and applicability of different kinds of fuel are influenced by the principles there elucidated.

The different kinds of fuel are all of vegetable origin, either directly or indirectly. In the different conditions of wood, peat, and coal, it is the ligneous tissue of plants that constitutes fuel; in each of these conditions there is a general similarity of elementary composition, accompanied by considerable differences in the relative proportions of the

elementary constituents, and by specific differences of character, apparently depending more upon the arrangement of those constituents than upon their actual amount.

The chief elementary constituents of fuel are carbon, hydrogen, and oxygen, together with a small proportion of nitrogen; and in all kinds of fuel there is, besides these constituents, a greater or less amount of earthy or inorganic substance, remaining as ash when the fuel is burnt, and originating partly from the plant-tissues, partly from their mechanical admixture with earthy substances. The amount of ash in fuel varies considerably, from less than 1 per cent. to 10, and even 20 per cent. in some instances; but, on the average, 5 per cent. of ash is as much as there should be in good fuel.

One of the most important points of difference between the various kinds of fuel consists in the amount of volatilisable substance they contain; and their applicability for various purposes depends in a great measure on this circumstance, as much as upon their respective capability of generating heat. Fuel which contains a large amount of combustible volatilisable substance, and gives rise to a copious evolution of hydrocarbon vapour and gases, burns with flame, while the more purely carbonaceous fuels, containing little or no volatilisable substance, burn without flame or with only a small flame. It has been very generally considered that fuel which possesses the character of burning with the largest flame is especially suitable for use in generating steam, and for evaporating, as well as for certain metallurgical operations; while the more carbonaceous kinds are generally found better adapted for iron smelting, and for producing high temperatures.

The presence of water in fuel is obviously objectionable, whether it be employed for evaporation or for producing high temperatures: for, in the one case, the vaporisation of the water contained in the fuel consumes an equivalent quantity of heat, and thus reduces the effect produced by the fuel; in the other case, the water-vapour produced tends to reduce the temperature obtainable by the combustion.

The amount of water in fuel may vary from nothing to 40 per cent. or more, and some kinds of fuel give rise to the production of a further portion of water than that which they actually contain. The great difference between the capability of fuel to produce high temperatures, according as it contains or produces water by combustion, has long been known, and the practice of kiln-drying and of charring fuel, is founded on the knowledge of this fact.

By charring or carbonising fuel, the whole of the water it contains, or is capable of producing, may be separated; and though a considerable portion of the carbon is also volatilised, partly in the state of hydrocarbon compounds, and partly as carbonic acid and carbonic oxide, the residual carbonaceous portion has, weight for weight, a greater capability of producing a high temperature than the raw fuel, and in some cases is otherwise more suitable for certain metallurgical operations.

The extent to which the volatilisation of carbon takes place, in carbonising fuel, depends greatly upon the mode in which the operation is conducted. As a rule, the yield of carbonaceous residue is greatest when the carbonisation is conducted rapidly. This is the case to the greatest extent with wood, which yields on the average 23 per cent. of charcoal by rapid charring, and only 14 per cent. by slow charring. In the carbonisation of coal, the difference is much less, and the amount of coke obtained, which varies very much, depends more upon the special character of the coal used.

**COAL.**—This is by far the most important of the materials employed as fuel. The varieties of coal are very numerous, and the differences between some varieties are very marked, though on the whole they are more differences of degree than of kind. According to these differences in the varieties of coal, they are generally divided into three classes, viz. 1. Anthracite; 2. Bituminous coal; and 3. Lignite; though, in many instances, it is not possible to recognise any absolute distinction between coals commonly referred to different classes.

There is an equal absence of any positive line of demarcation between coal and those more earthy combustible minerals, termed shales, with which it is usually associated; but from a practical point of view, the amount of earthy substance often constitutes a good criterion as to whether any particular mineral be suitable for fuel, and should consequently be regarded as coal. The determination of the question, even by this means, will sometimes be influenced by circumstances; thus, for instance, while 30 per cent. of ash in a combustible mineral of this description, might not prevent its being usefully employed as fuel at the place where it is raised, it would not be so regarded for the purpose of transport. From a variety of similar circumstances, the application of the term coal is entirely conventional. A scientific definition of coal is out of the question.

**Anthracite.**—The coals belonging to this class are characterised by containing a much larger amount of carbon than any other varieties, and but very little volatilisable substance.

## FUEL.

	South Wales. Regnault.	Glamorganshire. Wrightson.	South Wales. Vaux.
Carbon . . . . .	92.66	91.44	90.39
Hydrogen . . . . .	3.33	3.46	3.28
Oxygen . . . . .	2.63	2.68	2.98
Nitrogen . . . . .		0.21	0.83
Sulphur . . . . .		0.79	0.91
Ash . . . . .	1.68	1.52	1.61
	100.00	100.00	100.00
Coke . . . . .		92.90	

Anthracite is less readily combustible than almost any other kind of fuel; it requires a strong draught, and must be gradually heated before being thrown on the fire, otherwise it decrepitates and crumbles to powder, which stops the draught and causes much waste. When properly burned, it generates a very high local temperature, and is on that account especially adapted for melting furnaces.

*Bituminous Coal.*—The coals belonging to this class are characterised by containing a more or less considerable proportion of bituminous substance capable of being decomposed by heat, and yielding volatile, oily, and gaseous products. Some of these coals, when heated, undergo a kind of fusion, swelling up considerably as decomposition goes on, and leaving a bulky porous residue of carbon. These are called *caking coals*. Other bituminous coals do not present this character; but when heated, or in burning, retain their form, and split or open up into columnar fragments. These are commonly called *dry or freeburning coals*. The cannel coals, which properly belong to the bituminous class of coals, behave differently from either caking or dry coals when heated, though they burn most like the latter, and they are especially characterised by giving a very copious luminous flame.

In composition, bituminous coals generally are distinguished by containing a larger proportion of both hydrogen and oxygen than anthracite contains; but there is no recognised relation between their specific characters and their elementary composition. Even the property of caking seems to be more dependent on the constitution, than on the mere composition of the coals.

*Dry or Freeburning Coals.*

	Merthyr. How and Phillips.	Duffryn. Hqw.	Graigola. son.	Balcarres. Phillips.	Cwm Frood. How.	Hartley. How and Phillips.	Wolver- hampton. Vaux.	St. He- lena. Vaux.	Dalkeith Jewel. son.
Carbon . . . . .	90.37	88.26	84.87	83.54	82.25	81.18	78.57	75.41	74.55
Hydrogen . . . . .	4.12	4.66	3.84	5.24	5.84	5.56	5.29	5.22	5.14
Oxygen . . . . .	2.53	0.60	7.19	5.87	3.58	8.03	12.88	11.26	12.51
Nitrogen . . . . .	0.63	1.45	0.41	0.98	1.11	0.72	1.84	1.93	1.41
Sulphur . . . . .	1.20	1.77	0.45	1.05	1.22	1.44	0.39	0.90	1.33
Ash . . . . .	2.53	3.26	3.24	3.32	6.00	3.07	1.03	5.17	4.37
	101.28	100.00	100.00	100.00	100.00	100.00	100.00	101.01	102.51
Coke . . . . .	79.11	84.30	85.50	62.90	65.60	58.20	57.20	65.88	49.30
Ratio of volatile sub- stance to fixed carbon	0.27	0.19	0.17	0.62	0.57	0.75	0.76	0.55	1.10

*Caking Coals.*

	Oldcastle Fiery vein. Wrightson.	Tanfield. How and Phillips.	Mynydd Newydd. How.	Blaina. Noad.	Blaina. Noad.	Hedley's Hartley. How and Phillips.	Notting- ham. C. Tooke.	Trinidad. Tooke.
Carbon . . . . .	87.68	85.58	84.71	83.00	82.56	80.26	77.40	73.11
Hydrogen . . . . .	4.89	5.31	5.76	6.18	5.36	5.28	4.96	5.63
Oxygen . . . . .	3.39	4.29	3.52	4.58	8.22	2.40	7.77	17.08
Nitrogen . . . . .	1.31	1.26	1.56	1.49	1.65	1.16	1.55	0.87
Sulphur . . . . .	0.09	1.32	1.21	0.75	0.75	1.78	0.92	0.87
Ash . . . . .	2.64	2.14	3.24	4.00	1.46	9.12	3.20	3.61
	100.00	100.00	100.00	100.00	100.00	100.00	96.50	100.00
Coke . . . . .	79.80	65.10	74.80			72.20	63.20	54.00
Ratio of volatile sub- stance to fixed carbon	0.25	0.55	0.34			0.43	0.60	0.91

*Cannel Coals.*

	Wigan. Regnault.	Wigan. Vaux.	Tyneside. Taylor.
Carbon . . . . .	84.07	80.07	78.06
Hydrogen . . . . .	5.71	5.53	5.40
Oxygen . . . . .	7.82	8.10	3.12
Nitrogen . . . . .		2.12	1.86
Sulphur . . . . .		1.50	2.22
Ash . . . . .	2.40	2.70	8.94
	100.00	100.00	99.99
Coke . . . . .	59.00		
Ratio of volatile substance to fixed carbon	0.72		



**LIGNITE and BROWN COAL.**—The various kinds of combustible minerals to which these names are applied are but little employed as fuel in this country; but in the colonies they are of more importance. Lignite and brown coal are highly hygroscopic, and, in the air-dried condition, generally contain from 15 to 20 per cent. of water. In composition they approximate more or less to wood.

	Bovey.	Auckland. Tookev.	Tasmania. Tookev.
Carbon . . . . .	49·24 . . . . .	55·57 . . . . .	59·90 . . . . .
Hydrogen . . . . .	4·18 . . . . .	4·13 . . . . .	4·66 . . . . .
Oxygen . . . . .	16·97 . . . . .	15·67 . . . . .	15·99 . . . . .
Nitrogen . . . . .	0·41 . . . . .	0·15 . . . . .	1·08 . . . . .
Sulphur . . . . .	1·75 . . . . .	0·36 . . . . .	0·30 . . . . .
Ash . . . . .	1·69 . . . . .	9·00 . . . . .	4·64 . . . . .
Water . . . . .	25·75 . . . . .	14·12 . . . . .	13·43 . . . . .
	99·99 . . . . .	100·00 . . . . .	100·00 . . . . .
Coke . . . . .	30·80 . . . . .		
Ratio of volatile substance to fixed carbon . . . . .	2·38 . . . . .		

Wood is but little used as fuel except in countries where it is abundant, and where coal is scarce. The amount of water in wood varies considerably according to the kind of wood, and the time it has been kept. On the average, air-dried wood contains about 20 per cent. of water. The average composition of wood is

	Air dried.	Kiln dried, 140 C.
Carbon . . . . .	40·36 . . . . .	50·45 . . . . .
Hydrogen . . . . .	4·91 . . . . .	6·14 . . . . .
Oxygen . . . . .	32·66 . . . . .	40·83 . . . . .
Nitrogen . . . . .	·90 . . . . .	1·11 . . . . .
Ash . . . . .	1·17 . . . . .	1·47 . . . . .
Water . . . . .	20·00 . . . . .	
	100·00 . . . . .	100·00 . . . . .
Charcoal . . . . .	23·00 . . . . .	28·75 . . . . .
Ratio of volatile substance to fixed carbon . . . . .	2·95 . . . . .	2·64 . . . . .

**PEAT ; TURF.**—The chief obstacle to the use of peat and turf as fuel is the difficulty of obtaining them in a dry state. As they usually occur in bogs or mountain districts, they contain from 80 to 90 per cent. of water, and, even in the ordinary air-dried condition, the amount of water is not less than from 20 to 40 per cent.

The term turf is most correctly applicable to the more fibrous and spongy varieties of bog fuel, consisting, in great part, of mosses that have undergone but little alteration of structure.

The term peat should be restricted to those varieties in which the ligneous tissues of the mosses, &c., have been, to a more or less considerable extent, converted into a compact mass, which is sometimes as pasty as moist clay, and, when air-dried, presents much resemblance to some kinds of coal belonging to the lignite class.

The appearance and texture of air-dried peat and turf present great variations between these two extreme conditions, the most important points of difference being the density and the liability to absorb water. The density of air-dried turf is sometimes as low as 0·2 or about 12 lbs. per solid cubic foot; the density of peat is sometimes as much as 1·23 or about 78 lbs. per solid cubic foot. Turf will sometimes absorb more than its own weight of water, while good peat will not take up more than about 10 per cent.

In composition there is but little difference between turf and peat or the different kinds of each, but the amount of ash varies considerably, and is sometimes as high as 10, or even 20 per cent.

	Lewis turf, air-dried. Paul.	Peat, air-dried. Vaux.	Lewis peat, air-dried. Paul.	Lewis peat, kiln-dried. Paul.
Carbon . . . . .	35·3 . . . . .	43·3 . . . . .	46·1 . . . . .	60·0 . . . . .
Hydrogen . . . . .	3·6 . . . . .	4·1 . . . . .	4·6 . . . . .	6·9 . . . . .
Oxygen . . . . .	19·2 . . . . .	22·4 . . . . .	23·6 . . . . .	30·0 . . . . .
Nitrogen . . . . .	·7 . . . . .	1·8 . . . . .	1·0 . . . . .	1·3 . . . . .
Sulphur . . . . .	· . . . .	0·4 . . . . .		
Ash . . . . .	1·1 . . . . .	7·7 . . . . .	1·5 . . . . .	1·9 . . . . .
Water . . . . .	40·1 . . . . .	20·3 . . . . .	23·2 . . . . .	
	100·0 . . . . .	100·0 . . . . .	100·0 . . . . .	100·1 . . . . .
Charcoal . . . . .		29·3 . . . . .	31·5 . . . . .	39·0 . . . . .
Ratio of volatile substance to fixed carbon . . . . .		3·27 . . . . .	2·28 . . . . .	1·64 . . . . .

Of the elementary constituents of fuel, only the carbon and hydrogen are combustible, and capable, by their combustion, of contributing to the generation of heat. Consequently, the amount of heat generated by any kind of fuel, or its calorific power, depends upon the amount of carbon and hydrogen it contains. There being no absolute measure of heat, the calorific power of fuel can only be estimated relatively, by comparing the effects produced by equal weights of different kinds of fuel.

In the combustion of hydrogen, the amount of heat generated is always the same, but in the combustion of carbon, it differs according to the nature of the compound produced by the combustion. When carbon is fully oxidised and converted into carbonic acid, the amount of heat generated is much greater than when it is only converted into carbonic oxide, so that, as regards the use of fuel, carbon has two degrees of calorific power, corresponding to the two degrees of oxidation.

The quantity of heat generated by the combustion of hydrogen is 4.265 times as great as that generated by the combustion of an equal weight of carbon to carbonic acid, according to the most accurate determinations by Favre and Silbermann.

In expressing the calorific power of fuel, the amount of heat generated by the combustion of carbon to carbonic acid is taken as the standard of comparison. This calorific power of carbon is expressed as a definite quantity, by the number of parts by weight of water capable of being heated from a given temperature to a temperature 1° higher (4° to 5° C.), by the combustion of one part by weight of carbon. This numerical expression of calorific power will, of course, vary according as the thermometric scale to which it refers is that of Fahrenheit, Centigrade, or Reaumur, and it will vary in the same ratio as the degrees of those different scales bear to each other.

	Reaumur.	Centigrade.	Fahrenheit.	Relative calorific power.
Ratio of thermometric degrees . . . . .	0.8	1	1.8	
Calorific power of carbon . . . . .	1010	8080	14,544	1.000
Calorific power of hydrogen . . . . .	43,077.5	34,462	62,032	4.265

In this comparison of the calorific power of carbon and that of hydrogen, no particular unit of weight is referred to; it merely indicates that a pound, a grain, or a ton of carbon or of hydrogen will raise the temperature of as many pounds, grains, or tons of water from 4° to 5° C., as correspond with the number expressing their calorific power respectively for each thermometric scale. The unit of heat, or that quantity of heat which raises the temperature of the unit of weight of water from t° to t° + 1°, will vary according to the thermometric scale and the unit of weight to which it refers. According to the Centigrade scale and the French system of weights, the unit of heat is the quantity which raises the temperature of a kilogramme of water from 4° to 5° C., while the unit of heat for the Fahrenheit scale and the British system of weights is the quantity which raises the temperature of a pound of water from 40° to 41° F., and these two units bear the following relation to each other.

British unit of heat.		French unit of heat.
1	=	0.251996
3.96832	=	1.

It is important to bear in mind these differences of expression, inasmuch as they often have to be taken into account in calculations; but the expression of the relative calorific power of carbon and of hydrogen, as stated above, is not affected by them.

Since the calorific power of fuel, or its theoretical fuel value, depends on the amount of combustible carbon and hydrogen it contains, it follows that, the percentage composition of any particular fuel being ascertained by analysis, it is easy, by means of the data given for the relative calorific power of carbon and of hydrogen, to calculate the relative calorific power of the fuel, that of carbon being taken as unity. There are three possible cases which may obtain in regard to this calculation, viz.:

1. When the combustible portion of the fuel consists entirely of carbon, as in the case of coke or charcoal, the percentage of carbon in the fuel expresses its relative calorific power, as compared with pure carbon.
2. When the combustible portion of the fuel contains both carbon and hydrogen, the relative calorific power is found by multiplying the percentage amount of hydrogen by 4.265 and adding the product to the number expressing the percentage of carbon.
3. When the fuel contains, besides carbon and hydrogen, more or less oxygen, this constituent must be considered as already combined with an equivalent quantity of either carbon or hydrogen, which is consequently rendered ineffective for generating heat. In such cases, it is only the surplus carbon and hydrogen, over and above the quantity equivalent to the oxygen in the fuel, that can generate heat by combustion.

Consequently the greater the amount of oxygen in fuel, the smaller will be its relative calorific power. The presence of oxygen in fuel, acts in a twofold manner in reducing the calorific power; by reducing the actual amount of carbon and hydrogen, and also by rendering part of that amount ineffective for generating heat.

The influence exercised by the oxygen contained in fuel in diminishing the calorific power will also depend upon whether it is the carbon or hydrogen that is rendered ineffective in generating heat, and the conditions under which the fuel is burnt will determine, in great measure, which of these effects is produced.

Since in carbonic acid, oxygen is combined with three-eighths of its weight of carbon, and in water it is combined with one-eighth of its weight of hydrogen, the quantity of carbon rendered ineffective by a given quantity of oxygen would be three times as much as the quantity of hydrogen rendered ineffective by the same quantity of oxygen. According to the older determinations of the heat generated by the combustion of hydrogen and carbon, which made the calorific power of hydrogen just three times as great as that of carbon, the result obtained by calculation was the same in either case; but adopting the more accurate data afforded by the experiments of Favre and Silbermann, the result will differ in some instances considerably, according as it is assumed that hydrogen or carbon is rendered ineffective for generating heat.

The relative calorific power of fuel may be calculated by means of the following formulæ, in which  $p$  represents the relative calorific power; and  $C, H, O$  represent the amounts of carbon, hydrogen, and oxygen in one part of the fuel:

1. Fuel containing only carbon . . . . .  $p = C.$
2. Fuel containing carbon and hydrogen . . . . .  $p = C + 4.265 H.$
3. Fuel containing carbon, hydrogen, and oxygen  $\left\{ \begin{array}{l} p = C - \frac{3}{8}O + 4.265 H. \\ \text{or } p = C + 4.265 (H - \frac{1}{8}O). \end{array} \right.$

If it is desired to express the calorific power of fuel in heat-units, the amount of carbon and the amount of available hydrogen in one part of the fuel are to be respectively multiplied by the numbers expressing the calorific power of carbon and of hydrogen, and the sum of the two products represents the relative calorific power of the fuel in heat-units:

1.  $p = 8080 C.$  2.  $p = 8080 C + 34462 H.$  3.  $p = 8080 C + 34462 (H - \frac{1}{8}O).$

In the following table the relative calorific power of several combustible substances is given both as calculated by the above formulæ and as expressed in heat-units:

1 Fuel.	2 Composition of Fuel.					3 Weight of Oxygen for combustion.	4 5 6 Calorific power in heat-units.			7 Weight of water heated from the freezing-point to boiling.	8 Weight of water at 100° C. converted into steam.
	Carbon.	Hydrogen.	Oxygen.	Ash.	Water.		Relative.	Centigrade.	Fahr.		
HYDROGEN . . . .	...	1.00	...	...	...	8	4.265	34462	62032	344.62	62.658
MARSH GAS . . . .	0.75	0.25	...	...	...	...	1.816	14676	26416	146.75	26.682
OLEFANT GAS . . .	0.857	0.143	...	...	...	...	1.466	11849	21328	118.49	21.543
COAL:											
Average Welsh . .	0.838	0.048	0.041	0.049	...	...	1.020	8241	14833	82.41	14.983
" Newcastle . . .	0.821	0.053	0.037	0.038	...	...	1.017	8220	14796	82.20	14.945
<b>Carbon . . . . .</b>	<b>1.00</b>	...	...	...	...	<b>2.67</b>	<b>1.000</b>	<b>8080</b>	<b>14544</b>	<b>80.80</b>	<b>14.691</b>
COAL:											
Average Scotch . .	0.785	0.056	0.097	0.040	...	...	0.973	7861	14150	78.61	14.292
" Derbyshire . . .	0.797	0.049	0.101	0.026	...	...	0.986	7733	13919	77.33	14.060
" Lancashire . . .	0.779	0.053	0.095	0.049	...	...	0.955	7717	13860	77.17	14.031
PEAT:											
Average kiln-dried . . . }	0.60	0.060	0.307	0.020	...	...	0.694	5640	10152	56.40	10.254
Average air-dried . . . }	0.461	0.046	0.246	0.015	0.232	...	0.526	4250	7650	42.50	7.727
WOOD:											
Average dried at 140° C. . . }	0.503	0.061	0.407	...	...	...	0.551	4455	8029	44.55	8.100
Average air-dried . . . }	0.404	0.049	0.327	...	0.200	...	0.430	3547	6385	35.47	6.449
CARBONIC OXIDE . .	0.43	...	0.57	...	...	0.57	0.214	1731	3116	17.31	3.159



The numbers in column 7 are obtained by dividing those in column 5 by 100, or those in column 6 by 180, upon the assumption that equal quantities of heat are requisite for raising the temperature of  $x$  pts. of water  $y$  degrees, or  $y$  pts. of water  $x$  degrees. Thus the heat generated by the perfect combustion of one pound of carbon would be sufficient to raise the temperature of 8080 pounds of water from  $4^{\circ}$  to  $5^{\circ}$  C., or of 14,544 pounds from  $40^{\circ}$  to  $41^{\circ}$  F. or of 80.8 pounds of water from the freezing to the boiling point:

Quantity of water. 8080lbs.	x	Increase of temperature. $1^{\circ}$ C.	=	Quantity of water. 80.8lbs.	x	Increase of temperature. $100^{\circ}$ C.
or						
Quantity of water. 14,544lbs.	x	Increase of temperature. $1^{\circ}$ F.	=	Quantity of water. 80.8lbs	x	Increase of temperature. $180^{\circ}$ F.

This assumption is not strictly correct, since the specific heat of water increases slightly as the temperature increases beyond its point of greatest density; but the approximation is sufficiently near for ordinary calculations.

The numbers in column 8 are obtained by dividing the numbers in column 7 by 5.5, on the assumption that the quantity of heat requisite to convert water at the boiling point, into steam under the ordinary atmospheric pressure, is 5.5 times as much as would be requisite for raising the temperature of the same weight of water from the freezing to the boiling point.

Whatever mode of expressing the calorific power of fuel may be adopted, it must be remembered that the results obtained by any of the above formulæ are to be considered merely as representing the relative quantities of heat generated by the combustion of equal weights of the fuel and of the standard with which it is compared. The results so obtained do not represent either the relative value of fuel, or the thermal effect capable of being produced by its combustion.

The thermal effect of fuel, or the temperature of the fire, does not depend solely on the calorific power or the amount of heat generated by its combustion; but likewise on the quantity and nature of the products resulting from the combustion.

The total heat generated by the combustion of any fuel, is communicated to the products of combustion, which in all ordinary cases are gaseous, producing in them, at the moment of combustion, a temperature determined, partly by the calorific power of the fuel, and partly by the nature of the products of combustion. Thus, for instance, taking the simplest case, carbon requires for its combustion to carbonic acid, 2.67 times its weight of oxygen, producing 3.67 times its weight of carbonic acid, the temperature of which is raised, at the moment of combustion, above the original temperature of the oxygen, by the diffusion of the heat generated throughout the carbonic acid produced. The quantity of heat generated by the combustion of carbon is capable of raising the temperature of a quantity of water equal to 8080 times the weight of the carbon burnt, from  $4^{\circ}$  to  $5^{\circ}$  C., and would raise the temperature of a quantity of water equal to the weight of the carbonic acid, produced about  $2202^{\circ}$  C.

Parts by weight of water. 8080	x	Increase of temperature. $1^{\circ}$ C.	=	Increase of temperature. $2201^{\circ} \cdot 63$ C.	x	Parts by weight of water. 3.67
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But since the specific heat of water, or its capacity for heat, is much greater than that of carbonic acid, the increase of temperature in the carbonic acid produced by the combustion of carbon, is proportionately greater than the increase of temperature that would be produced in a quantity of water equal to 3.67 times the weight of carbon burnt.

The quantities of heat requisite to produce an equal increase of temperature in equal weights of carbonic acid and of water being in the proportion of 0.2614 : 1.0000, the quantities of heat requisite to raise the temperature of 3.67 pts. water and 3.67 pts. carbonic acid one degree are therefore as

Parts by weight of water. 3.67	x	Specific heat in heat-units. 1.000	:	Parts by weight of carbonic acid. 3.67	x	Specific heat in heat-units. 0.2614	=	3.67 : 0.794.
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Consequently the increase of temperature in the 3.67 pts. of carbonic acid, to which the heat generated by the combustion of 1 pt. carbon is communicated, at the moment of combustion, may be ascertained by dividing the number of heat-units by the quantity of heat which raises the temperature of the 3.67 pts. carbonic acid one degree:

$$\frac{8080}{0.794} = 10,174^{\circ} \text{ C.}$$

The heat generated in the combustion of hydrogen is sufficient to raise the temperature of a quantity of water equal to 34,462 times the weight of the hydrogen burnt

from  $4^{\circ}$  to  $5^{\circ}$  C.; but hydrogen requires for combustion 8 times its weight of oxygen, producing 9 times its weight of water-vapour. The quantity of heat generated is much greater than in the combustion of carbon; but the product of combustion through which that heat is diffused is nearly  $2\frac{1}{2}$  times as much as in the combustion of an equal weight of carbon. A portion of the heat generated by the combustion of hydrogen, becomes latent and ineffective for increasing the temperature of the product, being consumed in determining the vaporous condition of the water produced. The latent heat of water, or the quantity of heat requisite to convert 1 pt. of water at  $100^{\circ}$  C. into steam, is 537 times as much as is requisite to raise the temperature of an equal weight of water from  $4^{\circ}$  to  $5^{\circ}$  C. The quantity of heat that becomes latent in the 9 pts. water-vapour produced by combustion of hydrogen, will therefore be 4833 heat-units, which must be deducted from the total heat generated, in order to ascertain the quantity of heat available for producing increase of temperature.

	Parts by weight of water-vapour.	Heat units.
Total heat of combustion of hydrogen . . . . .		34,462
Latent heat of water in heat-units . . . . .	9 x 537 =	4,833
Available heat . . . . .		29,629

The specific heat of water-vapour being 0.475 as compared with that of water = 1.000, the quantities of heat requisite to raise the temperature of 9 pts. water and 9 pts. water-vapour are therefore as:

Parts by weight of water.	Specific heat in heat-units.	Parts by weight of water-vapour.	Specific heat in heat-units.	
9	1.000	9	0.475	= 9 : 4.275

And the increase of temperature produced will be  $6930^{\circ} \cdot 7$  C.:

$$\frac{29629}{4.275} = 6930^{\circ} \cdot 7 \text{ C.}$$

Hence as will be seen from the following comparison, thermal effect and calorific power are not necessarily equal; but, on the contrary, the thermal effect depends upon other circumstances, more than upon the calorific power of the fuel burnt.

	Weight.	Weight of oxygen.	Ratio.	Weight of products.	Ratio.	Heat units.	Ratio.	Thermal effect.	Ratio.
Carbon	1	2.67	1	3.67	1	8080	1.000	10174 $^{\circ}$	1.000
Hydrogen	1	8	3	9.00	2.4	34462	4.265	6930 $^{\circ}$	0.681

In both these instances, the combustion is supposed to have been effected in oxygen, and with only just as much as is chemically equivalent to the carbon and hydrogen burnt. But in all cases of the application of fuel, atmospheric air is the source of the oxygen that supports the combustion. The nitrogen it contains, in the proportion of 77 per cent., not only takes no part in the generation of heat, but, on the contrary, reduces the thermal effect below what it would be by combustion in oxygen.

In the combustion of carbon in air, the quantity of nitrogen in air containing 2.67 pts. by weight of oxygen is 8.94:

$$\begin{array}{c} \text{Atmospheric air.} \\ \text{O} \quad \text{N} \\ 23 : 77 = 2.67 : 8.94 \end{array}$$

The specific heat of nitrogen being 0.244, the quantity of heat requisite to raise the temperature of that quantity of nitrogen from  $4^{\circ}$  to  $5^{\circ}$  C. is

$$\begin{array}{ccc} \text{Parts by weight} & & \text{Heat-unit.} \\ \text{of nitrogen.} & & \\ 2.181 & = & 8.94 \times 0.244 \end{array}$$

And, adding to this the quantity of heat requisite to raise the temperature of the carbonic acid produced, as found above, the quantity of heat requisite for raising the temperature of the whole products of combustion in air from  $4^{\circ}$  to  $5^{\circ}$  C. will be

$$\begin{array}{ccc} \text{Heat-units.} & & \\ 2.976 & = & 2.181 + 0.794 \end{array}$$

And the increase of temperature produced will be

$$2715^{\circ} \text{ C.} = \frac{8080}{.976} = \frac{\text{total heat of combustion.}}{\text{quantity of heat requisite to heat the products and nitrogen from } 4^{\circ} \text{ to } 5^{\circ} \text{ C.}}$$

In the combustion of hydrogen in air, the quantity of nitrogen in air containing 8 pts. of oxygen is:

Atmospheric air.

$$26.78 : 8 = \frac{N}{77} : \frac{O}{23}$$

the quantity of heat requisite to raise its temperature from  $4^{\circ}$  to  $5^{\circ}$  C. is:

Heat-units.

$$6.534 = 26.78 \times 0.244$$

and the increase of temperature produced will be

$$2741^{\circ} \text{C.} = \frac{29629}{4.275 + 6.534} = \frac{\text{available heat of combustion.}}{\text{quantity of heat requisite to heat the products and nitrogen from } 4^{\circ} \text{ to } 5^{\circ} \text{ C.}}$$

The difference between the temperatures capable of being produced by the combustion of carbon and hydrogen in oxygen and in air is in both cases very considerable; but it is much greater in the case of carbon, since the amount of heat generated by its combustion is much less than that generated by hydrogen.

	Calorific power.	Ratio.	Temperature produced				Difference	Ratio.
			in oxygen.	Ratio.	in air.	Ratio.		
Carbon	8,080	1.000	10,174°	1.000	2715°	1.002	7459°	1.000
Hydrogen	34,462	4.265	6,930°	0.681	2741°	1.009	4189°	0.561

This comparison will suffice to show that, in all cases where high temperatures are required, it would be a great advantage to have an available means of increasing the amount of oxygen in the air supporting combustion; and that, in such cases, a very great saving of fuel might be effected by the use of oxygen, or of air containing a larger amount of oxygen than is present in atmospheric air.

There is another circumstance which influences the temperature capable of being produced by the combustion of fuel, and renders it less than would be indicated by the above calculation. In the combustion of fuel in a furnace, the conditions are such that, while at the outside the fuel is in contact with atmospheric air, there is within the furnace, a constant tendency to the production of an atmosphere consisting of carbonic acid, water-vapour, and nitrogen. To maintain the combustion of fuel, it is necessary not only to keep up a continual supply of air, but also to remove the gaseous products of combustion as they are formed. This is generally done by means of a draught, produced by a chimney; but, in any case, the gaseous products of combustion become mixed with the fresh supply of air, and exercise a great influence in reducing its efficacy in supporting combustion (i. 1101). Hence it is necessary to maintain an excess of oxygen in the atmosphere surrounding the fuel within the furnace, and, for this purpose, the quantity of air supplied must, in all ordinary cases of the use of fuel, be greater than that containing just enough oxygen to produce carbonic acid and water with the combustible constituents of the fuel burnt. In practice it is generally considered that the quantity of air requisite for the perfect combustion of fuel in ordinary furnaces, amounts to twice as much as that containing oxygen enough to convert its combustible constituents into carbonic acid and water.

In this way, the quantity of the products of combustion, through which the heat generated is distributed, is nearly doubled, and there is consequently a proportionate reduction of the temperature produced. In the case of carbon burnt with twice as much air as would be sufficient theoretically for its conversion into carbonic acid, the gaseous products of combustion would amount to 24.22 times the weight of the carbon burnt, and in the case of hydrogen to 80.56 times the weight of hydrogen burnt.

	Parts by weight of air.	Volume of air at 60° F. per pound of fuel, cubic feet.	Parts by weight of gaseous products.
Carbon	1 . . . 23.22	303.30	24.22
Hydrogen	1 . . . 79.56	908.62	80.56

The specific heat of air being 0.2377, the quantities of heat requisite for raising the temperature of these additional quantities of air from  $4^{\circ}$  to  $5^{\circ}$ , and the temperatures produced will be:

$$\begin{aligned} \text{Combustion of Carbon.} \quad 2.7696 &= 11.61 \times 0.2377 \quad \text{and} \quad 8.2672 = 34.78 \times 0.2377. \\ \text{Combustion of Hydrogen.} \quad 1408^{\circ} \text{C.} &= \frac{8080}{2.7696 \times 2.9755} \quad \text{and} \quad 1550^{\circ} \text{C.} = \frac{29629}{8.2672 \times 10.8093}. \end{aligned}$$

Hence it will be evident that the admission into a furnace, of more air than is requisite, will be attended with a proportionate waste of heat, and that it is desirable



always to effect combustion with the least sufficient supply of air. If the air be forced into the furnace by means of a fan or blast-pipe, as in a forge, fuel may be burnt with much less air than when it is drawn in by means of a chimney, and with greater economy of the heat generated. This economy may be effected to a greater extent with fuel which contains but little volatilisable substance.

The general formulæ for ascertaining the thermal effect of any kind of fuel from its composition are as follow :

$$T = \frac{\text{For Combustion in Oxygen.}}{c C + c' H - l W} \div \frac{\text{For Combustion in Air.}}{c C + c' H - l W} \\ = \frac{s \cdot 3 \cdot 67 C + 9 H + s' W}{s \cdot 3 \cdot 67 C + 9 H + s' W + s'' N + s''' A} A$$

Here  $T$  = increase of temperature produced by combustion.

$C$  and  $H$  = quantities of carbon and hydrogen available in 1 pt. by weight of the fuel.

$W$  = total quantity of water yielded by 1 pt. by weight of the fuel.

$l$  = latent heat of water.

$s, s', s'', s'''$  = specific heat of carbonic acid, water-vapour, nitrogen, and air.

$c$  and  $c'$  = calorific power of carbon and hydrogen.

$N$  = quantity of nitrogen in air necessary for converting combustible constituents of 1 pt. by weight of fuel into carbonic acid and water.

$A$  = extra quantity of air supplied for combustion.

The results obtained by these formulæ apply only to the perfect combustion of the combustible constituents of fuel into carbonic acid and water; and they express the highest possible capabilities of fuel as compared with pure carbon, and when burnt under the most favourable conditions.

But in all ordinary cases, the practical effect obtainable from fuel is much less than its relative capability as indicated by calculation. This is the case whether the effect to be produced be high temperature or vaporisation; and, in some cases, the practical effect may amount to only a small fraction of the calorific power or the thermal effect.

One of the most obvious, though by no means the most considerable, causes of the difference between the relative capability of fuel and the practical effects, consists in the waste of fuel as dust and cinders. With some kinds of fuel that are very brittle, such as anthracite and some of the Welsh steam coals, the waste due to this character may be very considerable, especially if the firing is improperly managed; but with care and with some kinds of fuel, the waste of fuel as dust and cinders may be very small.

Another cause of loss is imperfect combustion. This may be due to an insufficient supply of air, and the consequent production of carbonic oxide. At a sufficiently high temperature, carbonic acid combines with a further quantity of carbon, equal to that which it contains; but this combination is essentially different from the direct combination of carbon with oxygen. Though there is a true chemical change, it is not combustion, but is more analogous in its effects to the vaporisation of ice by superheated steam. Instead of heat being generated, it disappears, and the loss of heat resulting from this action may be very considerable, since the heat generated will only be that corresponding to the lower calorific power of carbon. Thus, for example :

	Heat-units.
The heat generated by the combustion of carbon to carbonic acid is . . . . .	8080
While the heat generated by the combustion of twice the weight of carbon } to carbonic oxide is . . . . .	4946
Loss of heat by production of carbonic oxide . . . . .	3134

This action will always take place, to some extent, when fuel is burnt in thick layers, and when it is burnt very rapidly in confined spaces, as in the furnaces of steam-vessels.

Imperfect combustion may also result from the presence of volatilisable substance in fuel. When fuel containing water, or volatilisable combustible substance, is first thrown upon a fire, heat is abstracted from the fire by the production of steam and hydrocarbon vapours. The temperature is thus considerably reduced. In the case of air-dried wood, more than three-fourths would be thus vaporised, and in the case of ordinary Newcastle coal, more than one-third, the vapour so given off from wood being chiefly water, and that from the coal consisting chiefly of hydrocarbons, as shown below :

One part by weight of yields vaporisable		Percentage composition.			
		Wood.	Coal.	Wood.	Coal.
C	.	·1853	·2522	24·38	64·10
H	.	·0083	·0460	1·10	11·80
HO	.	·5674	·0638	73·40	16·20
N, &c.	.	·0090	·0313	1·10	7·90
		·7700	·3933	100·00	100·00
Calorific power in heat units	.	1784	3623		

If the temperature in the furnace is sufficiently high, and these vapours are mixed with a sufficient proportion of atmospheric air, they will be burnt; but if the volatilisable portions were not burnt, the loss of calorific power would be in the case of wood, more than one-half, and in the case of coal nearly one-third.

When these hydrocarbon vapours burn, or come in contact with highly heated fuel, they are immediately decomposed, with separation of carbon in a very fine state of division; and if the temperature of the atmosphere within the furnace, be insufficient to determine the combination of the whole of this carbon with oxygen, some of it escapes unburnt, producing smoke and soot. In a flame of this kind, which burns without smoke, the deposition of unburnt carbon is immediately effected by reducing the temperature of the flame, as in holding a piece of cold metal in a gas-flame.

Then since the combustion of these vapours in a boiler furnace takes place just as the burning vapour is passing away from the fire, along the surface of the boiler towards the chimney, the abstraction of heat may be sufficient to reduce the temperature of the mixed gas below the point at which it would be capable of effecting the combustion of the suspended carbon. The carbon thus eliminated by the decomposition of the hydrocarbon vapours, and that prevented from being burnt in consequence of the cooling of the burning gas, is partly deposited as soot, and partly swept away mechanically by the gaseous products of combustion, giving rise to smoke.

The tendency to the production of soot and smoke in the combustion of fuel containing volatilisable substance will be greater in proportion to the amount of volatilisable substance in the fuel, and more especially in proportion to the amount of carbon in the vapour produced. In the case of Newcastle coal, the amount of carbon in the vapour is nearly three times as great as in the vapour from wood, and it is also in a condition likely to give rise to elimination of carbon.

This production of soot and smoke involves a corresponding loss of heat, and to prevent this loss, provision must be made for supplying a sufficiency of air for effecting the perfect combustion of the vaporous products, without reducing the temperature of the atmosphere in the furnace. This is generally done by introducing air through the furnace-door, above the fire, and at the back of the fire, so as to become heated before mixing with the vaporous products. Mechanical arrangements for supplying the fuel in continuous small portions to the furnace, have also been used with the same object.

The possible waste of heat resulting from the presence of volatilisable combustible substance in fuel, may be judged of by comparing the calorific power of Newcastle coal with that of the fixed carbon it contains. The average of Newcastle coal contains 60 per cent. of fixed carbon, so that if the coal be burnt in such manner that only this portion of it is effective in generating heat, its calorific power might be regarded as 0·60 as compared with carbon.

But this coal contains 82·12 per cent. carbon, and 4·60 per cent. available hydrogen; consequently its calorific power is

$$·8212 + (·046 \times 4·265) = 1·017;$$

and if the volatile products were not burnt at all, the waste of heat would amount to four-tenths, and if only the carbon of the volatile products remained unburnt, the waste would amount to nearly one-fourth.

The extent to which heat may be wasted in consequence of imperfect combustion from this cause, and the liability to the production of smoke and soot in the case of different kinds of fuel, may be seen from the following table:

	Welsh coals.	Average wood.	Peat.	Lancashire coal.	Derbyshire coal.	Newcastle coal.	Scotch coal.
Total carbon	63·78	40·36	60·6	77·90	79·68	82·12	78·53
Amount of carbon volatilised	15·09	18·53	19·0	22·56	23·01	25·72	28·31
.. .. available hydrogen	4·27	0·83	1·0	4·13	3·68	4·60	4·40

Whenever fuel is employed for generating steam or for analogous purposes, it is desirable to effect perfect combustion as far as possible; but there are some applications of fuel in metallurgical operations, where it is advantageous to have a highly carbonaceous flame, and where this is of greater importance than obtaining the full heating effect of the fuel. Thus, for instance, in the manufacture of malleable iron, it

is necessary that the body of flame and heated gases passing through the working chamber of the puddling furnace, should not contain free oxygen in sufficient quantity to oxidise, or, as it is technically termed, to "cut" the metal.

Besides the actual loss of heat in consequence of imperfect combustion, and in other ways, a large portion of the heat generated by the combustion of fuel is always consumed in producing the draught by which the products of combustion are removed from the furnace, and the fresh supply of air maintained. This portion of the heat is not available under ordinary circumstances for producing any other useful effects. The amount of heat so consumed varies according to the nature of the products of combustion, and according to the use to which the fuel is applied. In every case the whole quantity of heat corresponding to the temperature at which the gaseous products of combustion are discharged from the place where the heating effect is to be produced, is ineffective.

In boiler furnaces it has been found that, to maintain a sufficient draught by means of a chimney, the temperature of the gaseous products of combustion must not be reduced below  $315^{\circ}\text{C}$ . For example, the amount of heat thus consumed in the two extreme cases of the combustion of carbon and of hydrogen in twice as much air as is necessary for their conversion into carbonic acid and water vapour, will be:—

		Parts by weight, products of combustion.	Quantity of heat = $10^{\circ}$ in temperature of products. Heat units.		Temperature of products.	Heat units.
Carbon	. 1	= 24.22	5.735245	x	$315^{\circ}$	= 1807
Hydrogen	. 1	= 80.56	19.076526	x	$315^{\circ}$	= 6015

The amount of heat which thus passes away without producing its desired effect, will be proportionately greater as the temperature at which the products of combustion pass to the chimney, is higher than  $315^{\circ}\text{C}$ .; but it may be assumed that the minimum consumption of heat in producing a draught by means of a chimney, amounts in round numbers to one-fourth of the available heat generated. When the combustion of fuel is effected in this manner, its practical effect for heating and evaporation will therefore be only three-fourths of the capability indicated by calculation.

If the perfect combustion of fuel could be effected in boiler furnaces, with no more air than sufficient for converting its combustible constituents into carbonic acid and water vapour, the loss of heat from the circumstance just mentioned, might be reduced to one-half what it is when fuel is burnt with double that quantity of air. By using a fan-blower to drive the air into the furnace, instead of drawing it in by means of a chimney, the economy of heat might be carried still further, inasmuch as the gaseous products of combustion at, or even below,  $315^{\circ}\text{C}$ ., might then be employed for heating purposes, to which they cannot be applied when the heat they contain is required to produce a draught.

In reverberatory furnaces, the amount of heat which passes away in the gaseous products of combustion is very much greater than it is in boiler or evaporating furnaces, in consequence of the much higher temperature generally required to be maintained in those furnaces.

In the manufacture of malleable iron, the temperature at which the iron is required to be kept in puddling furnaces is about  $1650^{\circ}\text{C}$ . At that high temperature, the dispersion of heat by radiation and conduction is so great, that it is necessary to keep up a rapid current of heated gases through the working chamber of the furnace and a rapid combustion of fuel to maintain the temperature required. By the heating of the iron, the atmosphere in the furnace is rapidly brought below this temperature, and must be constantly replaced by fresh portions of gaseous products of combustion, heated above that temperature. It is only the heat corresponding to the difference between the temperature of the iron and the higher temperature of the atmosphere in the furnace, that is available for heating or for maintaining the temperature of the iron. The circumstance that the specific heat of iron is not much more than half as great as that of the atmosphere in the furnace, favours the heating of the iron; but, in any case, it is only part of this available heat that is really effective in raising or maintaining the temperature of the iron. The higher the temperature of the iron, the smaller will be the effective portion of the available heat, because, as the temperature rises, the dispersion of heat by radiation and conduction increases very considerably. Mr. Prideaux has estimated that even when the iron is first put into the puddling furnace, and with the furnace atmosphere at a constant temperature of  $1815^{\circ}\text{C}$ ., the effective portion of the available heat is not more than one-half of the whole, and that when the temperature of the iron is  $1370^{\circ}\text{C}$ ., less than one-eleventh of the whole is effective. In furnaces where welding heat is required, the amount of heat that is effective is still less, not being more than one-sixty-fourth of the whole heat generated, the remaining 63



parts being wasted. By increasing the temperature of the atmosphere in the furnace, and the difference between that temperature and the temperature to be maintained in the iron, so as to increase the rate of heating, a great economy of fuel may be effected, because, in that case, a greater amount of the available heat becomes effective. Thus, Mr. Prideaux shows that, if the atmosphere in a furnace, where a welding heat is required, be maintained at a temperature of  $2039^{\circ}\text{C}$ ., one-sixteenth of the heat generated will be effective instead of only one-sixty-fourth. In this case, an increase of temperature amounting to one-eighth is attended with a four-fold economy of heat.—B. H. P.

**FULLER'S EARTH.** *Walkerde. Walkthon.*—An argillaceous deposit occurring in connection with the chalk, oolite, &c. It is earthy, with a shining streak; greenish-grey, oil-green, white, yellowish, reddish or red-brown. Specific gravity = 1.7—2.4. It feels either greasy or harsh; adheres a little to the tongue; falls to pieces in water. It is found at Nutfield near Reigate in Surrey; near Maidstone in Kent, Woburn in Bedfordshire; at Vahls near Aix-la-Chapelle, Rosswein in Saxony, Zwickowitz in Bohemia, and elsewhere. (Dana, ii. 504.)

The term *fuller's earth* was originally confined to a sandy argillaceous earth met with in the upper part of the stratum just mentioned, on account of its use in *fulling* or cleansing cloth, when first woven, from grease and other impurities; but it is now extended to the entire formation to which this earth belongs. (See *Ure's Dictionary of Arts*, &c. ii. 307.)

**FULMINATES.**  $\text{C}^{\text{N}}\text{M}^{\text{O}}$  (M denoting a metal).—This name is applied to a class of salts polymeric with the cyanates and cyanurates, but distinguished from them by the property of detonating violently when heated or struck. Howard first showed (Phil. Trans. 1800) that nitrate of mercury or nitrate of silver heated with alcohol and excess of nitric acid, yields a peculiar, crystalline, easily detonating precipitate, viz. *fulminating mercury* or *fulminating silver*; but the composition of these precipitates remained unknown till 1824, when it was discovered by Liebig (Ann. Ch. Phys. [2] xxiv. 298; Ann. Ch. Pharm. xxvi. 646), whose determination was afterwards confirmed by Gay-Lussac (Ann. Ch. Phys. [2] xxv. 285).

Fulminic acid, or fulminate of hydrogen, has not been obtained; and the only fulminate of which a satisfactory analysis has been made, is the silver-salt, which, according to Gay-Lussac and Liebig, contains 7.92 per cent. carbon, 9.24 nitrogen, 72.19 silver, and 10.65 oxygen, agreeing with the empirical formula  $\text{CNAgO}$ , which requires 8.00 carbon, 9.33 nitrogen, 72.00 silver, and 10.67 oxygen. This is the formula of cyanate of silver. But there can be no doubt that the formula of fulminate of silver is a multiple of this, and most probably  $\text{C}^{\text{N}}\text{Ag}^{\text{O}}$ : for, in the first place, the fulminates are formed by the action of nitric acid and a nitrate on alcohol, which is a 2-carbon compound; secondly, many of the reactions of the silver-salt show that one-half of the silver is in a different state from the other half; and thirdly, several double fulminates are known, including a fulminate of silver and hydrogen,  $\text{C}^{\text{N}}\text{AgHO}$ . Hence Gay-Lussac and Liebig assigned to neutral fulminate of silver the formula  $\text{Cy}^{\text{N}}\text{Ag}^{\text{O}}$ , supposing it to be derived from a dibasic fulminic acid,  $\text{Cy}^{\text{H}}\text{H}^{\text{O}}$ . This view is supported by the fact that in many reactions of fulminating silver, hydrocyanic acid is produced.

Berzelius (*Berz. Jahresber.* xxiv. 89) supposed that the fulminates contain a metallic nitride, *e. g.* fulminating silver =  $\text{AgO}.\text{AgN}.\text{C}^{\text{N}}\text{NO}$ , this mode of representation being intended to afford an explanation of the fact that, in many reactions of fulminating silver, only half the silver is separated; also that fulminate of silver and potassium,  $\text{KO}.\text{AgN}.\text{C}^{\text{N}}\text{NO}$ , detonates as strongly as fulminating silver itself, the detonation in either case being attributed to the sudden decomposition of the compound  $\text{AgN}$ .

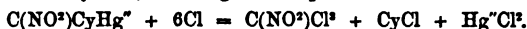
The formation of the fulminates by the action of nitric acid upon alcohol, together with their explosive properties, induced Laurent and Gerhardt (*Précis de Chimie organique*, ii. 445) to regard them as compounds containing nitril,  $\text{NO}$ , a radicle which is frequently introduced into organic molecules by the action of nitric acid, and almost always imparts to them more or less of an explosive character; they accordingly represented fulminating silver by the formula  $\text{C}^{\text{N}}(\text{NO})\text{Ag}^{\text{O}}$ .

This view of the composition of the fulminates receives strong confirmation from the recent experiments of Kekulé (Ann. Ch. Pharm. ci. 200; *cr.* 279), and of Schischkoff (*ibid.* ci. 213), which have shown: 1. That fulminating mercury, treated with chlorine, or with hypochlorite of calcium, yields chloropiricrin, a compound certainly containing the radicle nitril, viz.  $\text{C}(\text{NO})\text{Cl}$  (i. 923); and with bromine, it yields dibromonitracetone,  $\text{C}^{\text{N}}(\text{NO})\text{Br}^{\text{N}}$ , or bromopiricrin,  $\text{C}(\text{NO})\text{Br}$ , according as the fulminating mercury or the bromine is in excess.—2. Fulminuric or isocyanuric acid,  $\text{C}^{\text{N}}\text{H}^{\text{O}}$ , a compound produced by the action of alkaline chlorides or iodides on fulminating

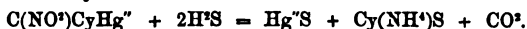
mercury (p. 738), also yields chloropicrin when treated with hypochlorite of calcium, and trinitracetonitrile,  $C^3(NO^3)^3N$ , when treated with strong nitric acid. Schischkoff has also observed that when the same acid is decomposed by zinc in presence of a mineral acid, the hydrogen eliminated from the latter is almost wholly absorbed. This reaction, together with the explosive character of the fulminates, also points to the existence of an oxide of nitrogen in these compounds; and this being the case, the mode of formation of fulminuric acid shows that the nitro-compound must also exist in fulminic acid.

Kekulé assigns to fulminic acid the formula  $C(NO^2)(CN)H^2$  or  $C(NO^2)CyH^2$ , which amounts to supposing: 1. That half the carbon and half the nitrogen in fulminic acid are so arranged as to yield cyanogen-compounds under the influence of certain reagents.—2. That the remaining half of the nitrogen exists in fulminic acid in the same form as in the so-called nitro-compounds. This view is in accordance with the following reactions.

Fulminating mercury, suspended in water and treated with chlorine gas, yields chloropicrin, gaseous chloride of cyanogen, and chloride of mercury, without any evolution of carbonic anhydride, according to the equation:



Fulminating mercury treated with sulphydric acid yields sulphocyanate of ammonium and carbonic anhydride:



According to Kekulé's formula, fulminic acid belongs to the same type as marsh-gas, and exhibits a very close analogy with the bodies in the following series [ $NO^2 = X$ ]:

Marsh-gas . . . . .	CH H H H.
Chloride of Methyl . . . . .	CH H H Cl.
Chloroform . . . . .	CH Cl Cl Cl.
Nitroform . . . . .	CH X X X.
Chloropicrin . . . . .	CX Cl Cl Cl.
Chloride of Dinitromethylene . . . . .	CX X Cl Cl.
Acetonitrile . . . . .	CH H H Cy = $C^2H^3N$ .
Trichloroacetonitrile . . . . .	CCl Cl Cl Cy = $C^2Cl^3N$ .
Trinitroacetonitrile . . . . .	CX X X Cy = $C^2X^3N$ .
Dibromonitracetonitrile . . . . .	CX Br Br Cy = $C^2XB^2N$ .
Fulminating Silver . . . . .	CX Ag Ag Cy = $C^2XAg^2N$ .
Fulminic acid ( <i>hyp.</i> ) . . . . .	CX H H Cy = $C^2XH^2N$ .

According to these formulæ, the compounds to which fulminic acid is most intimately related are chloropicrin and acetonitrile; its formula is in fact the same as that of mononitracetonitrile.

The formation of fulminic acid by the action of nitrous acid upon alcohol may be explained as follows. On the one hand cyanic acid is formed:

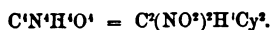


on the other, nitro-acetic acid; and these two compounds by their mutual action produce fulminic acid:



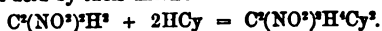
Kekulé regards the formation of fulminating mercury as analogous to that of chloroform. In the one case, alcohol is subjected to the simultaneous action of oxidising and chlorinising agents; in the other, the alcohol is likewise oxidised (converted into cyanic acid), while, at the same time, cyanogen and mercury are present and ready to take the place which the chlorine occupies in chloroform, the strong nitric acid likewise introducing the group  $NO^2$ . In fact, fulminating mercury might be regarded as nitrated chloroform in which 2 at. Cl are replaced by mercury and one by cyanogen. This view receives some corroboration from the fact that the analogous compound, chloropicrin, is produced by adding chloride of sodium to a mixture of alcohol and strong nitric acid.

Schischkoff (Compt. rend. li. 99) doubles the preceding formula of fulminic acid, but otherwise agrees with Kekulé in supposing that it contains both cyanogen and nitril:



According to this formula, the acid may be regarded as derived from ethylic alcohol, by the substitution of cyanogen for oxygen ( $Cy^2$  for  $O$ ), and of 2 at. nitril for 2 at. hydrogen. Schischkoff further supposes, that when alcohol is acted upon by nitric

acid, dinitroethylene,  $C\left\{\begin{smallmatrix} H \\ (NO)_2 \end{smallmatrix}\right\}$  (not yet isolated), and hydrocyanic acid are formed, and produce fulminic acid by their union:

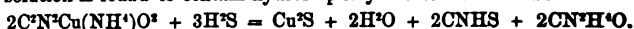


In like manner, a fulminate may be regarded as a compound of a metallic cyanide with dinitroethylene in which the hydrogen is replaced by an equivalent quantity of a metal: a view which accords with the fact that in the double decomposition of fulminates, e.g. of the silver-salt by potash, only half the metal is separated.

Schischkoff formerly regarded fulminic acid as a compound of 2 at. cyanic acid and 1 at. nitracetonitrile =  $(CHNO)^2.NC(NO)_2H^2$  (Ann. Ch. Pharm. ci. 213; Gm. xii. 551).—[For Gentile's views of the constitution of the fulminates, see J. pr. Chem. lxxxiv. 101; Rép. Chim. pure, 1862, p. 195.]

**Fulminate of Copper** is obtained in green crystals, very slightly soluble in boiling water and highly explosive, by boiling fulminating mercury with water and copper, and filtering the hot liquid. When fulminating silver is used instead of the mercury-salt, a greenish-blue powder is obtained, less explosive, and likewise very slightly soluble in water, forming a sky-blue solution.

**Fulminate of Copper and Ammonium**,  $C^2N^2\left\{\begin{smallmatrix} Cu \\ NH \end{smallmatrix}\right\}O^2$ .—Formed by mixing a solution of fulminate of copper with a large excess of ammonia, 1 at. copper being then replaced by 1 at. ammonium. When a stream of sulphuretted hydrogen is passed through the solution of this salt, the copper is completely precipitated, and the filtered solution is found to contain hydrosulphocyanic acid and urea:



The formation of urea from this salt exhibits in a striking manner the close relation between the fulminates and cyanates. (Gladstone, Ann. Ch. Pharm. lxi. 1.)

**Fulminate of Copper and Potassium**.—By digesting fulminate of silver and potassium with copper, the silver is precipitated and a liquid obtained, which is neither precipitated by potash, nor turned blue by ammonia, unless it be previously mixed with hydrochloric acid. (Liebig.)

**Fulminate of Hydrogen, or Fulminic Acid**, does not appear to exist in the free state.

**Fulminate of Mercury. Mercuric fulminate. Fulminating Mercury**.—This salt, discovered by Howard, is produced when mercury or mercuric oxide is heated with alcohol and strong nitric acid; also by boiling fulminating silver with mercury and water, and by precipitating the zinc-salt with solution of mercuric chloride.

To prepare it, 1 pt. of mercury is dissolved in 12 pts. nitric acid of specific gravity 1.3; and the solution, when cold, is mixed with 11 pts. alcohol of 85 to 88 per cent., and the mixture is heated in the water-bath. It then enters into ebullition, and must be removed from the fire as soon as it begins to show turbidity, then left to cool, decanted, and the mercuric fulminate collected on a filter and purified by recrystallisation from boiling water. The mother-liquor yields a fresh quantity by evaporation (Chevalier, Ann. Ch. Pharm. xxiii. 167). The reaction by which this compound is produced, is attended with the evolution of a white cloudy vapour, the *ethereal nitrous gas* of the older chemists, containing nitrogen and its oxides, carbonic acid, hydrocyanic acid, aldehyde, acetic acid, acetic ether, formic acid, formic ether, a large quantity of nitrous ether, &c., together with vapour of mercury. The nature and quantity of these products varies according to the proportions of the mixture, the duration of the action, the degree of heat employed, &c.

Cloez found in the mother-liquors of the preparation a peculiar acid, called *homolactic acid* (q. v.), resembling lactic acid.

Mercuric fulminate crystallises in white silky needles, soft to the touch, having a sweetish metallic taste, highly explosive, very slightly soluble in cold, more soluble in boiling water, soluble in ammonia.

**Decompositions**.—1. Fulminating mercury heated to 186° C., or forcibly struck, detonates with great violence; the explosion is likewise produced by contact with strong sulphuric or nitric acid, by a spark from flint and steel, or by the electric spark. When moist, it may be handled without risk of explosion, but in the dry state it is a most dangerous substance, and all manipulations performed upon it should be conducted with the greatest caution.

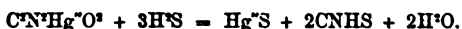
10 grains of fulminating mercury yield, when exploded, 4 cubic inches of permanent gas at 0° C., and 29.5 in. bar.; but at the moment of explosion this volume is greatly augmented by the expansion produced by the heat of the explosion, and by the admixture of mercurial vapour. The explosive force within a small space is much greater than



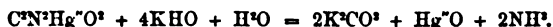
that of gunpowder, but, at the same time, it is more sudden, and therefore not so well adapted for propelling a ball, being, in fact, more likely to burst the gun: for propelling a ball, a gradual expansive force is required, such as will continue its impulsive action on the projectile during the whole time of its passage along the bore of the gun. Fulminating mercury is, however, admirably adapted, by its ready inflammability, for the priming of percussion caps, for which purpose it is prepared on the large scale:—1 kilogramme of mercury yields, by the preceding process,  $1\frac{1}{2}$  kilogrammes of fulminate, which will serve for priming 40,000 caps. (Gerh. ii. 364; see also *Ure's Dictionary of Arts, &c.*, ii. 308.)

2. Hot *nitric acid* decomposes fulminating mercury, yielding carbonic acid, acetic acid, and mercuric nitrate.—3. Moderately dilute *sulphuric acid* decomposes it without detonation, but with rise of temperature and evolution of gas. In this reaction, 84 per cent. of a white non-detonating powder is separated, apparently a mixture of metallic mercury with mercurous oxalate (mercurous sulphate, according to Berthollet), whilst also a small quantity of mercury appears to remain dissolved in the liquid containing the sulphuric acid.

4. Aqueous *hydrochloric acid* decomposes fulminating mercury, without any considerable evolution of gas, forming mercuric chloride and mercurous oxalate (Howard). According to Ittner, it produces a large quantity of hydrocyanic acid.—5. *Sulphydric acid* converts fulminating mercury immersed in aqueous ammonia into sulphide of mercury and hydrosulphocyanic acid (Pagenstecher):



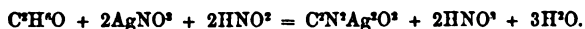
6. Boiling *potash-solution* separates a large quantity of mercuric oxide, without evolution of ammonia, and yields a filtrate, which, as it cools, deposits yellow detonating flakes and needles, probably consisting of potassio-mercuric fulminate, and forms with nitric acid a white precipitate, which detonates strongly by percussion. *Baryta, strontia, and lime* behave like potash (Liebig). According to Pagenstecher (Br. Arch. vii. 293), potash-ley exerts no action in the cold; when hot, it separates mercuric oxide, but the filtrate yields by evaporation, not a detonating salt, but only carbonate of potassium. This reaction might be represented by the equation:



7. A solution of fulminating mercury in warm aqueous ammonia deposits, on cooling, yellow, strongly detonating, granular crystals; but if the solution be boiled for some time, it deposits, on cooling, a yellowish white, non-detonating powder (Liebig). According to Pagenstecher, fulminating mercury dissolves abundantly in ammonia, without separation of oxide; the solution, when exposed to the air, gives off ammonia, and becomes covered with a crystalline crust of unaltered fulminating mercury, which renews itself as often as it is broken.

8. Finely divided *zinc, copper, or silver* (the last in contact with platinum-foil), boiled in water with fulminating mercury, decomposes that compound, yielding metallic mercury and fulminate of zinc, copper, or silver (Liebig). A pasty mixture of fulminating mercury with pulverised *iron* and water, moderately warmed, becomes strongly heated, and dries up almost completely to a red-brown mass; this, when mixed with lukewarm water and filtered, yields a filtrate which, on evaporation, leaves a small saline residue containing ammonia; and on the filter there remains a black-brown residue which contains globules of mercury; yields prussian blue with hydrochloric acid; and when heated after drying, burns with bright sparkling, but without detonation. (Pagenstecher.)

**Fulminates of Silver.**—1. The *neutral salt, or fulminating silver, C<sup>N</sup>Ag<sup>2</sup>O*, is formed by heating aqueous nitrate of silver with strong nitric acid and alcohol, the same phenomena and products appearing as in the formation of fulminating mercury (p. 732). Neutral nitrate of silver does not yield fulminating silver when boiled with alcohol; the formation of that compound requires the presence of nitrous acid, inasmuch as cyanogen is thereby produced; when nitrous acid vapour is passed into an alcoholic solution of nitrate of silver, fulminating silver quickly separates in large needles, without ebullition of the liquid (Liebig, Ann. Ch. Pharm. v. 287):



2. Fulminating silver is also produced by boiling fulminating mercury with water, pulverised silver, and platinum-filings. (Liebig.)

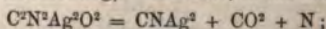
*Preparation.*—Nitrate of silver is heated with alcohol and strong nitric acid till the liquid begins to boil up; and the crystals of fulminating silver which form during the ebullition and as the liquid cools, are collected on a filter, washed with cold water, and dried either in the cold, or at most at the heat of the water-bath.

Howard and Cruickshank dissolve 1 pt. of silver in a mixture of 24 pts. water and 24 pts. of the strongest nitric acid, add 24 pts. of alcohol, and obtain 1.5 pt. of fulminating silver. Brugnatelli (A. Gehl. i. 665) pours 5 pts. alcohol and then 5 pts. fuming nitric acid on 1 pt. of pulverised lunar caustic, and at the proper time cools the mixture, which boils up and deposits fulminating silver, with water, to prevent the fulminating silver from being decomposed. Accum recommends 2.5 pts. of fuming nitric acid and 7 pts. of alcohol to 1 pt. of nitrate of silver. Descotils (Ann. Chim. lxii. 198) adds the alcohol to the nitric acid as the silver dissolves in it; as however the alcohol interferes with the solution of the silver, the product is, according to Liebig, greatly diminished thereby. Wagenman (Gibb. Ann. xxxi. 110) mixes a solution of 1 pt. silver in 8 pts. nitric acid of specific gravity 1.18, heated to 50° or 60° C., with 8 pts. alcohol of specific gravity 0.85; heats the liquid again to 50° or 60°, and adds 4 pts. of fuming nitric acid, which causes foaming and formation of fulminating silver in quantity at least equal to  $\frac{2}{3}$  of the silver used. According to Liebig, the quantity of alcohol here recommended is too small; and the liquid becomes too hot, whereby the fulminating silver is decomposed (Liebig). Gay-Lussac and Liebig dissolve 1 pt. of silver in 20 pts. nitric acid of specific gravity 1.308; add to the solution 27 pts. alcohol of 86 per cent.; heat the mixture till it boils up; remove the liquid, which is becoming turbid, from the fire; mix it, in order to moderate the frothing, with another 27 pts. of alcohol; and obtain, after the liquid has completely cooled, about 1 pt. of fulminating silver. The mother-liquor of fulminating silver is green if the silver contains copper, and when evaporated deposits all the copper in the form of oxalate; there then remains a liquid containing silver, which, when further evaporated, leaves a red salt, easily soluble in water. (Liebig.)

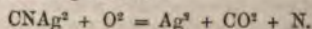
The preparation of fulminating silver requires the greatest caution. Capacious vessels must be used, so that the liquid may not boil over, as in that case the salt might dry on the outside and then explode; all flame must be removed to a distance, lest the vapours should take fire; and the mixture must be stirred with wooden rods, not with glass rods or other hard bodies. Contact with hard bodies must especially be avoided after the preparation is dry. Paper shovels must be used to transfer it, and it must be kept in vessels of paper or paste-board, not of glass, and the vessels must be loosely covered, as an explosion might arise from the friction of glass stoppers, or from pressing the cover of the box to fix it.

Fulminating silver forms small, white, opaque, shining needles, having a strong, bitterish metallic taste, and very poisonous. It is but very slightly soluble in cold water, dissolves in 36 pts. boiling water, and separates on cooling. It dissolves much more freely in aqueous ammonia, and is left behind unaltered as the ammonia evaporates. It is used for making crackers and other detonating toys.

*Decompositions.*—1. Fulminating silver gradually blackens when exposed to white or to blue light, giving off carbonic anhydride and nitrogen, and leaving a black substance, mixed with a small quantity of the undecomposed salt (Liebig).—2. It explodes much more violently than fulminating mercury, by heat, by the electric spark, by friction or percussion, or by contact with oil of vitriol. A heat of 100° to 130° C. is not sufficient to induce the explosion of dry fulminating silver; and it does not explode by mere pressure, unless the pressure be very strong. In the moist state, it requires a much harder blow to explode it than when dry, but it will sometimes explode, even under water, by friction with a glass rod. It explodes with peculiar readiness when rubbed with glass-dust or sharp sand; also, when dry, with the edge of a playing card. It may, however, be rubbed to powder in a porcelain mortar with a cork or with the finger (Liebig). When well washed, and then exposed to the sun till it is dry, it explodes on the slightest touch. According to Schmidt (Schw. J. xli. 72), oil of vitriol causes moist fulminating silver to detonate as strongly as the dry compound. The light accompanying the explosion, which is most easily seen in the dark, is reddish-white with a tinge of blue; it is succeeded by a grey vapour having a peculiar electrical odour. Gunpowder mixed with fulminating silver is not ignited by the explosion, but merely scattered about (Liebig). Fulminating silver, mixed with 20 times its weight of finely pulverised sulphate of potassium, gradually decomposes when heated in a tube, yielding 2 vols. carbonic anhydride to 1 vol. nitrogen (also carbonate of ammonia, if moisture is present), and doubtless leaves paracyanide of silver,  $\text{CNAg}^+$ ; for the residue mixed with cupric oxide and ignited again yields the same gaseous mixture, in about the same quantity and the same proportions as by the first ignition (Gay-Lussac and Liebig). Therefore, in the first instance:



afterwards, when ignited with cupric oxide:



A mixture of 1 pt. fulminating silver and 40 pts. cupric oxide, when heated, immediately gives off, without detonation, the whole of the carbonic anhydride and nitrogen gases in the proportion by vol. of 2 to 1. (Gay-Lussac and Liebig.)

3. Fulminating silver thrown into a bottle filled with *chlorine* explodes before it reaches the bottom, and therefore does not burst the bottle (E. Davy). Fulminating silver, well moistened with water and exposed to a current of chlorine gas, absorbs a large quantity of the gas, turns yellow, and is finally converted, without any formation of carbonic or chloric acid, into chloride of silver and a yellow oil, heavier than water, having a pungent odour, attacking the eyes strongly, and having a sharp burning taste which almost paralyses the tongue. If the mixture be agitated with water and distilled, gas is given off before the water begins to boil, and a colourless oil passes over, having a somewhat less powerful odour. This oil gives off gas under water, is insoluble in aqueous alkalis, but dissolves in alcohol; and the alcoholic solution, if mixed first with potash, then with a ferric salt, and then with an acid, exhibits a green colour. This oil is therefore related to chlorocyanic oil (p. 282). (Liebig, Pogg. Ann. xv. 564.)

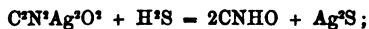
4. *Nitric acid* boiled for some time with fulminating silver decomposes it, forming nitrate of ammonia and nitrate of silver.

5. Dilute *sulphuric* or *oxalic acid* decomposes fulminating silver without effervescence, forming hydrocyanic acid and ammonia. (Gay-Lussac and Liebig.)

6. Aqueous *hydrochloric acid* immediately converts all the silver of fulminating silver into chloride of silver, with evolution of the odour of hydrocyanic acid (Descotils). By a comparatively small quantity of hydrochloric acid, the fulminating silver is converted into chloride and acid fulminate of silver,  $C^2N^2HAgO^2$ ; but on adding hydrochloric acid till the filtrate is no longer clouded by it, the acid fulminate is converted into chloride of silver, hydrocyanic acid, and a peculiar chlorinated acid (*chlorhydrocyanic acid*), containing a quantity of chlorine which appears to amount to 2.5 times as much as that which is contained in the chloride of silver produced. This acid tastes pungent and sweetish, reddens litmus strongly, and does not precipitate nitrate of silver. It decomposes when exposed to the air for some hours, more quickly when heated, yielding ammonia, which neutralises the still undecomposed portion of the acid. After neutralisation with potash, whereby it first acquires a rose-red, then a yellow colour, or after it has been saturated with ammonia by spontaneous decomposition, it colours ferric salts deep red. The acid saturated with potash, gives off ammonia when evaporated, and leaves a residue which effervesces strongly with acids, and whose aqueous solution precipitates nitrate of silver (Gay-Lussac and Liebig, Ann. Ch. Phys. xxv. 285).

7. Aqueous *hydriodic acid* decomposes fulminating silver in a similar manner, yielding iodide of silver and an iodated acid, analogous to the chlorinated acid, but forming a deep red precipitate with sesquichloride of iron, without being first neutralised; no odour of hydrocyanic acid is perceptible in this reaction (Gay-Lussac and Liebig). *Hydrofluoric acid* does not decompose fulminating silver.

8. A small quantity of aqueous *sulphydic acid* decomposes fulminating silver, forming sulphide of silver and cyanic acid; a larger quantity forms sulphide of silver and hydrosulphocyanic acid:



and

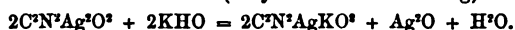


9. Aqueous solutions of *alkaline sulphides*, e. g. protosulphide of barium, acting in insufficient quantity, decompose cyanide of silver, yielding a fulminate of silver and the alkali-metal, and sulphide of silver (Liebig):

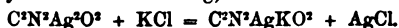


With a larger proportion of the metallic sulphide, an alkaline fulminate ( $C^2N^2K^2O^2$ ) appears to be formed at ordinary temperatures, and, with the aid of heat, a compound of the alkali with a sulphuretted acid different from hydrosulphocyanic acid.

10. Aqueous solutions of the *fixed alkalis*, as also *magnesia*, boiled with fulminating silver, gradually separate not quite half the silver in the form of a black oxide, a solution of fulminate of silver and potassium, sodium, barium, strontium, calcium, or magnesium being formed at the same time (Gay-Lussac and Liebig):



11. Aqueous solutions of the *alkaline chlorides*, even when added in excess, precipitate only half the silver in the form of chloride, and form fulminate of silver and potassium, &c. (Gay-Lussac and Liebig):





At the boiling heat, alkaline chlorides and iodides convert fulminic acid into fulminuric acid. (Liebig, Schischkoff; see p. 738.)

12.. *Copper or mercury*, boiled with fulminating silver and water, ultimately separates all the silver in the metallic state, forming fulminate of copper or fulminate of mercury (Liebig). When the boiling with mercury is continued for a short time only, fulminate of silver and mercury is formed. *Zinc*, even when boiled for several days with fulminating silver, separates only half the silver, so that fulminate of silver and zinc is formed. When fulminate of silver is boiled with water and *iron filings*, a red-brown filtrate is obtained, which, when evaporated, yields reddish laminated crystals of fulminate of iron. (Liebig.)

*Fulminate of Silver and Ammonium*.  $C^2N^2Ag(NH^4)O^2$ .—From a solution of fulminate of silver in hot aqueous ammonia, this salt crystallises on cooling in white, shining, crystalline grains, having a pungent metallic taste, while argentate of ammonia remains in solution. It detonates with three times the force of fulminating silver, and with extreme facility, even under the liquid, when touched with a glass rod; if, however, the liquid contains excess of ammonia, the explosion does not extend throughout the mass. It is very sparingly soluble in water. (Liebig.)

*Fulminate of Silver and Barium*.—Dingy white crystalline grains, which detonate with violence, dissolve sparingly in water, and are decomposed by hydrochloric acid. Zinc immersed in the boiling aqueous solution throws down silver; the filtrate deposits on evaporation a yellow powder, which between  $160^\circ$  and  $160^\circ$  C. burns away without detonation, like cyanate of silver, leaving carbonate of barium mixed with zinc, and when treated with hydrochloric acid, yields sal-ammoniac with effervescence, and cannot therefore be a fulminate. (Liebig.)

*Fulminate of Silver and Calcium*.—Small yellow crystalline grains, of high specific gravity, and dissolving readily even in cold water. (Liebig.)

*Fulminate of Silver and Hydrogen*, or *Acid Fulminate of Silver*,  $C^2N^2AgHO^2$ .—Precipitated in the form of a white powder, on mixing the aqueous solution of fulminate of silver and potassium with nitric acid not in excess:



This salt dissolves readily in boiling water, crystallising out on cooling; reddens litmus. By boiling with silver-oxide, it is converted into neutral fulminate of silver, and by boiling with mercuric oxide, into fulminate of silver and mercury. (Liebig, Ann. Ch. Phys. xxiv. 302.)

*Fulminate of Silver and Magnesium*.—*a. Basic*.—Obtained by boiling fulminating silver with magnesia and water. Rose-coloured powder, insoluble in water, which merely decrepitates when heated, giving off carbonic acid and ammonia, and leaving a residue of magnesia and silver.—*b. Neutral*.—White, thread-like crystals, resembling capillary native silver, and detonating strongly. (Liebig.)

*Fulminate of Silver and Mercury*, or *Argento-mercuric Fulminate*.—Formed by boiling fulminate of silver and hydrogen with mercuric oxide and water, or by boiling fulminating silver for not too long a time with mercury and water. From the filtrate the compound crystallises in small shining needles. (Liebig.)

*Fulminate of Silver and Potassium*,  $C^2N^2AgKO^2$ .—300 pts. (1 at.) fulminating silver are decomposed by not quite 74.6 pts. (1 at.) chloride of potassium dissolved in water; or water in which fulminating silver is suspended is kept in a state of ebullition, and aqueous chloride of potassium added as long as it occasions turbidity, but no longer; the liquid is then decanted from the chloride of silver, and cooled till it crystallises. If it be filtered instead of being decanted, a brownish liquid is obtained which yields brownish crystals; but if it be boiled for some time after dilution with water, it loses its colour, deposits black flakes, and when decanted from these, yields colourless crystals. The compound is obtained less pure by boiling fulminating silver with aqueous potash, and decanting from the precipitated oxide of silver.

It forms white, shining, somewhat elongated laminae, which have a repulsive metallic taste, and do not blue reddened litmus paper; detonates very easily and with great violence. It dissolves in 8 pts. of boiling, and in a larger quantity of cold water. Nitric acid added, not in excess, to the aqueous solution, throws down a white powder, consisting of fulminate of silver and hydrogen. Hydrochloric acid added to the solution mixed with potash, throws down a precipitate, which continues to redissolve in the liquid till all the potassium is converted into chloride; any further quantity of the acid throws down chloride of silver, with simultaneous formation of hydrocyanic acid, carbonic acid, and sal-ammoniac. Chloride of potassium does not decompose this salt. Copper immersed in the aqueous solution, throws down all the silver by forming fulminate of copper and potassium. The solution does not precipitate ferric sulphate, or yield prussian blue on subsequent addition of hydrochloric acid. (Liebig.)

*Fulminate of Silver and Sodium*, prepared by a similar process, forms small, red-brown, metal-shining laminae, more soluble in water than the potassium-salt, but otherwise exhibiting similar reactions. (Liebig.)

*Fulminate of Silver and Strontium*.—Dingy white crystalline grains, which detonate with violence, and are sparingly soluble in water. (Liebig.)

*Fulminate of Silver and Zinc*.—By boiling fulminating silver with zinc and water—whereby only half the silver is precipitated, even after long-continued ebullition—and evaporating the yellow filtrate, yellow detonating crystals are obtained, together with a yellow non-detonating powder. (Liebig.)

**Fulminates of Zinc** The neutral salt, also called *fulminating zinc*, was first obtained by Liebig, who showed that when zinc is boiled with fulminating mercury and water, mercury is separated, and a yellow liquid produced, which, on cooling, deposits yellowish, slightly detonating crystals; and was more particularly examined by E. Davy (Dublin Soc. Transact. 1829). To prepare it, 1 pt. of fulminating mercury is placed under water in contact with 2 pts. of zinc filings, and the whole frequently shaken, till all the mercury is precipitated and an amalgam formed, after which the filtrate is left to evaporate spontaneously.

The salt forms transparent, colourless, rhombic tables, which are tasteless, detonate very strongly at  $196^{\circ}$  C. or by percussion, or by contact with oil of vitriol,—are insoluble in water, but dissolve in aqueous alkalis. If the filtrate be evaporated, not in the cold, but at a gentle heat, there remains a deep yellow crust, together with yellow needles, which do not detonate by contact with sulphuric acid, but when heated, detonate as readily, but not so violently, as the first-mentioned crystals; this latter product is insoluble in cold water and alcohol, but dissolves sparingly in boiling water and very readily in ammonia.—An aqueous solution of fulminate of zinc poured into a bottle filled with chlorine gas yields a volatile, strongly smelling oil, which has a sweet and bitter taste, does not detonate, is insoluble in water, and reddens litmus after some time only.

*Fulminate of Zinc and Hydrogen, or Acid Fulminate of Zinc*.—The aqueous solution of fulminating zinc, recently prepared by the action of zinc on fulminating mercury, is precipitated by excess of baryta-water, which separates a large quantity of oxide of zinc; the excess of baryta is removed by a stream of carbonic acid; the filtrate, which contains fulminate of zinc and barium, and throws down fulminate of silver from a solution of the nitrate, is treated with the exact quantity of sulphuric acid required to remove the barium; and the liquid is filtered. The filtrate contains a large quantity of zinc. (Fehling, Ann. Ch. Pharm. xxvii. 130.)

The reaction is as follows:



then:



finally:



The solution has a powerful odour, like that of hydrocyanic acid; tastes agreeably sweet at first, but afterwards pungent and astringent. When kept in a bottle, it gradually loses its odour, becomes yellow, and deposits a yellow powder, but still forms an explosive yellow precipitate with nitrate of silver. (E. Davy.)

By saturating the solution with different bases, the double salts of fulminating zinc are obtained, in which the hydrogen is replaced by an equivalent quantity of another metal or of ammonium [they were regarded by Davy as pure fulminates]. These salts detonate, according to Davy, between  $176^{\circ}$  and  $230^{\circ}$  C.; most of them are soluble in water, and have a sweetish rough taste; their solutions precipitate nitrate of silver.

**Aluminium-salt**.—Yellow, indistinctly crystalline, neutral, slightly detonating, easily soluble.

**Ammonium-salt**.—The solution evaporated to a syrup, solidifies in the crystalline form. The salt has an alkaline reaction, deflagrates with a yellow flame when heated, and on exposure to the air, becomes moist, but does not decompose.

**Barium-salt**.—Crystallises from the syrupy solution in flat, transparent, four-sided prisms, which are alkaline, explode like the potassium-salt, turn yellow when exposed to the air, and are soluble in alcohol. (E. Davy.)

**Cadmium-salt**.—White opaque needles, which slowly turn yellow on exposure to the air, more quickly when heated, are very explosive, sparingly soluble in water.

**Calcium-salt**.—Very small, alkaline, detonating crystals, which turn yellow when heated, become moist when exposed to the air, and are sparingly soluble in water.

**Chromic-salt**.—Small, yellow-green, detonating crystals, easily soluble in water.

*Cobalt-salt*.—Delicate yellow needles, detonating, sparingly soluble in cold, more soluble in boiling water.

*Gold-salt*.—Obtained by precipitating a solution of fulminate of zinc and barium with a dilute solution of chloride of gold. Brown explosive powder, soluble in ammonia, hydrochloric acid, and strong sulphuric acid. The solution in sulphuric acid yields, when diluted with water, a dark purple precipitate; and the liquid filtered therefrom yields, by evaporation, besides a deposit of metallic gold, hexagonal prisms, which are explosive, insoluble in water and in hydrochloric acid, but soluble in nitro-hydrochloric acid.

*Lead-salt*.—White crystalline powder.

*Magnesium-salt*.—Long, flat, four-sided prisms, which are opaque; neutral; explode by heat or percussion, but not by contact with oil of vitriol; and dissolve readily in water and in alcohol.

*Manganese-salt*.—Viscous, very explosive mass.

*Nickel-salt*.—Yellow, or yellowish green crust, very explosive, slightly soluble in water.

*Palladium-salt*.—Brown explosive precipitate, insoluble in water.

*Platinum-salt*.—Obtained by decomposing fulminate of zinc and barium with sulphate of platinum. Brown precipitate which explodes without detonation; the filtered liquid yields, by evaporation, small yellowish brown prisms which detonate very strongly.

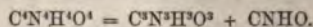
*Potassium-salt*.—Transparent, colourless, rhombic prisms, which have an alkaline reaction, and a sweetish rough taste; explode violently with a pale red flame, by heat, percussion, or contact with oil of vitriol; deliquesce in the air; but are insoluble in alcohol. (E. Davy.)

*Sodium-salt*.—Efflorescent, oblique rhombic prisms with dihedral summits. Detonates like the potassium-salt.

*Strontium-salt*.—Small, transparent needles.

**FULMINIC ACID.** See FULMINATES (p. 730).

**FULMINURIC ACID.**  $C^2H^2N^2O^2$ . *Isoeyanuric acid*.—An acid isomeric with cyanuric acid, which appears to have been discovered, independently and about the same time (1855), by Liebig (Ann. Ch. Pharm. xcv. 282), and by Schischkoff (Petersb. Acad. Bull. xiv. 98; Ann. Ch. Pharm. xcvii. 53). It is produced by the action of alkaline chlorides or iodides at the boiling heat on fulminating mercury, 3 at. fulminic acid (containing 2 at. carbon), being converted into 2 at. fulminuric acid, according to Liebig:  $3C^2N^2H^2O^2 = 2C^2N^2H^2O^2$ ; or according to Schischkoff, 1 at. fulminic acid (containing 4 at. carbon) being resolved into 1 at. fulminuric and 1 at. cyanic acid:



Schischkoff originally regarded fulminuric acid as a compound of 1 at. cyanic acid and 1 at. nitraceonitrile =  $CNHO.NC(NO^2)H$ : subsequently (Compt. rend. li. 99), he has expressed its composition by the formula  $N \begin{Bmatrix} C^2(NO^2)H^2O \\ Cy \\ H \end{Bmatrix}$

*Preparation*.—1. *Of the Ammonium-salt*.—Well washed fulminating mercury (60-75 grms.) is mixed in a glass flask with 700 to 800 cub. cent. of water, 60 cub. cent. of a cold-saturated solution of sal-ammoniac then added, and the whole heated to the boiling point. In a few minutes, a yellow crystalline powder begins to separate. As soon as the deposition of this precipitate has ceased, the vessel is removed from the sand-bath, and caustic ammonia added as long as a white precipitate is formed, after which the liquid is immediately filtered and evaporated to the crystallising point. The yellow crystals thus obtained are washed with water, and afterwards with alcohol, then dissolved in hot water, and the solution decolorised by well-washed blood-charcoal, or bone-charcoal. The filtrate on cooling yields dazzling white crystals of great beauty. (Liebig.)

2. *Of the Potassium-salt*.—Liebig prepares this salt in the same manner as the ammonium-salt. Schischkoff's mode of preparation is as follows:

2 pts. of moist fulminating mercury are added by small portions, and with constant stirring, to a nearly saturated and gently boiling solution of 1 pt. chloride of potassium, the ebullition being continued till no more fulminating mercury remains at the bottom. The liquid, which has a yellow colour, arising from the formation of a precipitate of indefinite constitution, is then filtered hot, in order that the principal product, a compound of fulminate of potassium with mercuric oxide, which is a curdy substance, sparingly soluble in cold water, may not be deposited during the filtration; and the yellow precipitate on the filter is washed with hot water. The filtrate, on cooling, deposits the curdy compound of mercuric oxide and fulminate of potassium, a further quantity



of which may be obtained by concentrating and cooling the mother-liquor and the wash-water. The portions which separate out in the second and third coolings are contaminated with the yellow precipitate, but may be purified by solution in boiling water. Ultimately a mother-liquor is obtained, containing an excess of chloride of potassium and a considerable quantity of mercuric chloride. To obtain the fulminate of potassium from the curdy compound, water is poured upon the latter, and sulphydric acid gas passed through the liquid, whereupon sulphide of mercury separates, together with crystals of the potassium-salt; and to obtain the latter, the entire liquid is heated, filtered hot, and left to crystallise. On cooling, it deposits shining colourless crystals of the potassium-salt, a further quantity of which may be obtained by repeatedly evaporating and cooling the mother-liquor. In this manner, 150 pts. of fulminating mercury yield 20 pts. of fulminate of potassium (Schischkoff). Liebig makes no mention of the curdy compound of mercuric oxide and fulminate of potassium. The reason of Schischkoff's having obtained it, is probably that he used a saturated solution of chloride of potassium, whereas Liebig used a dilute solution. Liebig's method is evidently the easier of the two.

From the potassium- or ammonium-salt, the lead or silver-salt may be prepared by double decomposition, and the free acid may then be obtained by decomposing the lead-salt with sulphydric, or the silver-salt with hydrochloric acid.

*Properties.*—The aqueous solution of the acid left to evaporate in a warm place, solidifies to a compact, yellowish, indistinctly crystalline mass (Liebig; Schischkoff). From a saturated alcoholic solution, the acid separates, according to Schischkoff, in small colourless prisms; Liebig, on the other hand, did not obtain crystals from the alcoholic solution. The crystals are anhydrous, and permanent in the air (Schischkoff). The solution has an acid reaction, and a very sour taste. It dissolves very easily in water; the solution in a small quantity of water forms a syrup, and may be evaporated without decomposition (Liebig). The acid is soluble in boiling alcohol (Liebig); in alcohol and in ether (Schischkoff).

*Decompositions.*—1. The acid and its salts explode when heated, the decomposition of the acid taking place at  $150^{\circ}\text{C}$ . (Schischkoff); the acid detonates slightly when heated (Liebig).—2. The aqueous solution of the acid is decomposed by boiling with mineral acids, a salt of ammonia being formed, carbonic anhydride evolved, and a brown substance produced, which has not been further examined (Liebig). Sulphuric acid decomposes the salts of fulminuric acid without blackening, forming sulphate of ammonia, and eliminating a mixture of carbonic anhydride and carbonic oxide. Weak hydrochloric acid has scarcely any action on the fulminurates; but the strong acid decomposes them, with formation of ammonia and evolution of carbonic anhydride. On saturating the excess of hydrochloric acid with an alkali, and adding a calcium or barium salt, a white precipitate is formed; but if the action of the hydrochloric acid has been long continued, and the liquid has been afterwards evaporated to dryness, no such precipitation takes place.—3. Nitrous acid passed through a solution of fulminuric acid, decomposes it, with evolution of gas (carbonic anhydride), and forms an acid which does not precipitate calcium-salts, but yields with nitrate of silver an insoluble salt containing nitrogen.—4. Caustic potash heated with fulminuric acid or its salts, gives off a large quantity of ammonia, and forms carbonate of potassium; and the solution, when neutralised by an acid, forms no precipitate with chloride of calcium or nitrate of silver.—5. Caustic baryta, heated with fulminuric acid or its salts, decomposes them, with evolution of ammonia and formation of a white precipitate containing carbonate of barium. This precipitate dissolves in hydrochloric or nitric acid; and after the excess of acid has been neutralised by ammonia, a precipitate is formed, probably identical with that which is produced on adding a barium salt to fulminuric acid which has been decomposed by hydrochloric acid (Schischkoff).—Sulphydric acid and sulphide of potassium have no action on fulminurates, even at the boiling heat.

*Fulminurates.* Fulminuric acid appears to be monobasic; at all events, all the fulminurates hitherto obtained contain only 1 at. metal in place of hydrogen.

*Fulminate of ammonium*,  $\text{C}^2\text{N}^2\text{H}^2(\text{NH}^4)\text{O}^2$ .—The preparation of this salt has already been described. It forms monoclinic crystals isomorphous with the potassium-salt, and having  $a : b : c = 1 : 1.8205 : 2.4015$ . Angle of inclined axes =  $79^{\circ} 6'$ . The crystals are prismatically elongated in the direction of the orthodiagonal, and are bevelled at the ends by the faces  $-P$ . Inclination of  $\text{oP} : +\text{P} = 120^{\circ} 6'$ ;  $\text{oP} : -\text{P} = 133^{\circ} 58'$ ;  $-P : -P$  in the clinodiagonal principal section =  $74^{\circ} 42'$  (Rammelsberg, Jahresber. d. Chem. 1857, p. 289). The crystals possess great refractive and dispersive power, and exhibit double refraction (Liebig, Rood). Dispersive power = 0.1006 nearly. For a perpendicularly incident ray, the angle of refraction of the extraordinary ray =  $4^{\circ} 22'$ . The acute angles of the crystals exhibit prismatic colours, in consequence of their high dispersive power. They also exhibit a splendid scarlet colour, arising from the superposition of the coloured

images of the ordinary and extraordinary rays, the violet of the first falling on the red of the second; the beauty of the red is moreover heightened by the neutralisation of the yellow (Rood, Ann. Ch. Pharm. xcv. 291). The crystals are anhydrous; when heated, they fuse, blacken, and give off hydrocyanic acid, ammonia, and afterwards hydrated cyanic acid, which, combining with the ammonia, forms in the upper part of the tube, a solid crystalline mass of urea (Liebig). The salt sustains a heat of  $150^{\circ}$  C. without alteration, but above that temperature it explodes like the other fulminates (Schischkoff). It dissolves sparingly in cold, readily in hot water; is insoluble in alcohol and ether. (Liebig.)

*Fulminate of Barium*,  $C^2N^2H^2BaQ^2 + aq$ .—Obtained by double decomposition in the form of a crystalline pulp composed of short, thin, white needles, which dissolve completely in a very large quantity of hot water, and separate on cooling in hard isolated crystals, which are colourless and transparent, and often take the form of rhombic prisms, terminated by a macrodiagonal dome (Liebig). According to Rammelsberg, the salt forms monoclinic crystals, exhibiting the faces  $\alpha P$ ,  $+P\infty$ ,  $-P\infty$ ,  $\alpha P$ ,  $[P\infty]$ , and prismatically elongated in the direction of the principal axis. Ratio of axes  $a : b : c = 1 : 2.032 : 2.348$ . Angle of inclined axes =  $72^{\circ} 27'$ ;  $\infty P : \alpha P$  in the clinodiagonal principal section =  $54^{\circ} 36'$ ;  $\alpha P : \infty P = 97^{\circ} 57'$ ;  $\alpha P : +P\infty = 120^{\circ} 36'$ ;  $\alpha P : -P\infty = 140^{\circ} 48'$ ;  $\alpha P : [P\infty] = 114^{\circ} 0'$ . The crystals refract doubly, but in a much less degree than the ammonium and potassium-salts, the angle of refraction of the extraordinary ray for perpendicular incidence being only  $1^{\circ} 9'$  (Rood). Between  $150^{\circ}$  and  $180^{\circ}$  C. they give off 8.52 per cent. (1 at.) water, and become opaque; at a higher temperature, they decompose like the potassium-salt. (Liebig.)

*Fulminate of Calcium* is soluble in water and in alcohol. (Liebig.)

*Fulminate of Copper* has not been prepared. An ammoniacal fulminate,  $2NH^2.C^2N^2H^2CuO^2$ , or *fulminate of ammoniacum*,  $C^2N^2H^2[NH^2(NH^2)Cu]O^2$ , is obtained by mixing fulminuric acid with a solution of a copper-salt in excess of ammonia and heating the liquid to boiling. The liquid, as it cools, deposits the salt in beautiful, shining, dark blue prisms, which undergo no change in the air at ordinary temperatures, or even at  $150^{\circ}$  C., but are decomposed, with explosion, at higher temperatures. It is nearly insoluble in water, and very sparingly soluble in ammonia, so that very small quantities of fulminuric acid may be separated in this form. (Schischkoff.)

*Fulminate of Ethyl*.—When fulminate of potassium is immersed in alcohol, and hydrochloric acid gas passed through the liquid, chloride of potassium is formed, together with fulminuric ether; as soon as the reaction is complete, the stream of gas must be discontinued, because an excess of hydrochloric acid decomposes the ether, with formation of a crystalline body. After the excess of alcohol and the chloride of ethyl formed at the same time have been distilled off, and a sufficient quantity of water has been added to the solution of chloride of potassium, the fulminuric ether separates in the form of an aromatic liquid; the portion which remains dissolved may be separated by agitating the watery liquid with common ether. Fulminuric ether is decomposed by alcoholic potash, even at ordinary temperatures, with formation of fulminate of potassium; it cannot be distilled without decomposition. Its alcoholic solution mixed with phenylamine deposits, after a few days, colourless, silky prismatic crystals, which melt and turn brown at  $100^{\circ}$  C., and perhaps consist of the phenylamide of fulminuric acid. (Schischkoff.)

*Fulminate of Iron (ferrosus)*, separates in beautiful, pale green crystals on heating a fulminate with ferrous acetate. (Schischkoff.)

*Fulminate of Lead*.—Neutral lead-salts are not precipitated by the alkaline fulminates. A basic lead-salt,  $Pb^2O.2C^2N^2H^2PbO^2$ , is obtained on adding basic acetate of lead to a solution of the fulminate of an alkali-metal, as a white crystalline precipitate, which dissolves in boiling water and separates in hard yellowish crystals on cooling. When decomposed by sulphydric acid, it yields fulminuric acid. (Liebig.)

The *fulminates of Lithium and Magnesium* are soluble in water and in alcohol.

*Fulminate of Mercury*.—The acid is not precipitated by mercurous or mercuric salts. Mercuric oxide heated in a solution of the acid dissolves in it, and the liquid on cooling deposits a mass resembling the curdy compound of mercuric oxide with fulminate of potassium. (Schischkoff.)

*Fulminate of Potassium*,  $C^2N^2H^2KO^2$ .—This salt, the preparation of which has been already described, forms long prisms, having a strong lustre and great refracting power (Liebig). A hot saturated solution, rapidly cooled, solidifies, from formation of a mass of very small silky needles; but by gentle evaporation, the salt is obtained in large and very regular crystals isomorphous with the ammonia-salt (Schischkoff). According to Rammelsberg (*loc. cit.*), they exhibit the faces  $\alpha P$ ,

$\infty P\infty$ ,  $oP$ ,  $+P\infty$ ,  $-P\infty$ ,  $-2P$ , and are prismatically elongated in the direction of the orthodiagonal. Ratio of axes  $a:b:c = 1:1.8704:2.3113$ . Angle of inclined axes  $= 83^\circ 32'$ ;  $\infty P$ :  $\infty P$  in the clinodiagonal principal section  $= 56^\circ 34'$ ;  $oP$ :  $\infty P = 93^\circ 4'$ ;  $oP$ :  $+P\infty = 125^\circ 2'$ ;  $oP$ :  $-P\infty = 132^\circ 51'$ .

The crystals are doubly refracting, and for perpendicular incidence, the angle of refraction of the extraordinary ray is between  $5^\circ$  and  $6^\circ$  (Rood, *loc. cit.*). They are anhydrous (Liebig). The salt when heated exhibits a faint glow, and gives off a small quantity of gas, like a mixture of an organic substance with nitre. It undergoes no change at  $226^\circ C.$ , but at a higher temperature it melts, gives off a large quantity of hydrocyanic acid, and afterwards becomes black, and explodes with a red flame. When slowly decomposed in a covered crucible by a heat gradually raised to redness, it yields pure white cyanate of potassium mixed with cyanide (Schischkoff). Heated with chloride of potassium in a combustion-tube, it gives off hydrocyanic acid, then carbonate of ammonia, and a gaseous mixture containing 2 vol. carbonic anhydride to 1 vol. nitrogen, like the gas evolved by the decomposition of dry fulminate and cyanate of silver mixed with sulphate of potassium. The residue consists of cyanide of potassium mixed with chloride (Liebig). The salt is less soluble in cold water than the ammonia-salt (Liebig, Schischkoff), but dissolves in hot water as easily as the latter (Liebig). It dissolves in 10 pts. of cold and a much smaller quantity of boiling water, but is insoluble in alcohol and ether. (Schischkoff.)

**Fulminate of Silver.**—A hot solution of fulminate of ammonium or potassium mixes with nitrate of silver without turbidity, but as the liquid cools, fulminate of silver separates from it in long, very thin needles, having a silky lustre (Liebig, Schischkoff). The crystals retain their lustre at  $100^\circ C.$ , and do not diminish in weight (Liebig). The salt is not blackened by light, and does not undergo any change at  $150^\circ$ , but at a higher temperature it explodes without noise, and gives off hydrocyanic acid (Schischkoff). It is decomposed by heat in the same manner as cyanate of silver (Liebig). It dissolves very sparingly in cold, but with moderate facility in boiling water, and may be recrystallised without alteration. (Liebig, Schischkoff.)

**Fulminate of Sodium** is more soluble than the potassium-salt, and crystallises from the aqueous solution by slow evaporation in long prisms. (Schischkoff.)

**Fulminate of Strontium** forms monoclinic crystals, exhibiting the combination  $+P$ .  $-P$ .  $oP$ .  $\infty P\infty$ . Ratio of axes  $a:b:c = 1:2.718:3.468$ . Angle of inclined axes  $= 82^\circ 50'$ ;  $+P$ :  $+P$  in the clinodiagonal principal section  $= 47^\circ 42'$ ;  $-P$ :  $-P$  in the same  $= 53^\circ 4'$ ;  $+P$ :  $-P$  in the orthodiagonal principal section  $= 140^\circ 49'$ ; in the basal section  $= 149^\circ 28'$ ;  $oP$ :  $+P = 102^\circ 57'$ ;  $oP$ :  $-P = 107^\circ 35'$ .

**FULMINURIC ETHER.** See FULMINURATE OF ETHYL (p. 740).

**FUMARAMIDE.**  $C^H^N^O^2 = N^2 \left\{ \begin{matrix} (C^H^O^2) \\ H^2 \end{matrix} \right\}$ . (Hagen, Ann. Ch. Pharm.

xxxviii. 276.)—A compound formed by the action of ammonia on fumarate of ethyl, and deposited in white scales, when the ether, mixed with aqueous ammonia, is set aside for some time in a cold place. It is insoluble in cold water, but dissolves in boiling water and separates out unchanged on cooling. It is insoluble in alcohol. (Hagen.)

Fumaramide yields by dry distillation, ammonia, a crystalline sublimate, and a carbonaceous residue. Heated with aqueous alkalis, it gives off ammonia, and when heated for some time with water, it is converted into fumarate of ammonium:



**Compound of Fumaramide with Mercuric Oxide.**—Red oxide of mercury boiled in water with fumaramide is rapidly decolorised, and yields a white pulverulent compound, which must be carefully washed with boiling water and dried at  $100^\circ$ . It is decomposed by hydrochloric and sulphydric acids. (Dessaignes, Ann. Ch. Pharm. lxxxii. 233.)

**FUMARIC ACID.**  $C^H^O^4 = (C^H^O^2) \left\{ \begin{matrix} H^2 \\ O^2 \end{matrix} \right\}$ . *Lichenic acid.* *Paramaleic acid.* (Lassaigne [1819], Ann. Ch. Phys. [2] xi. 93.—Pfaff, Schw. J. xlvii. 476.—Winckler, Repert. Pharm. xxxix. 48, 368; xlvi. 39, 363.—Pelouze, Ann. Ch. Phys. [2] lvi. 429.—Schödlér, Ann. Ch. Pharm. xvii. 148.—Rieckher, *ibid.* xlix. 31.—Delffs, Pogg. Ann. lxxx. 436.—Dessaignes, J. Pharm. [3] xxxii. 48.)—An acid isomeric with maleic acid, differing from maleic acid by containing 1 at. less of water, and from succinic acid by containing 2 at. less of hydrogen. It exists ready formed in several plants, viz. *Fumaria officinalis*, *Corydalis bulbosa*, *Glaucium flavum*, *Lichen islandicus*, and *Bolus pseudo-ignarius*. It is produced by the dehydration of maleic acid; by molecular transformation of maleic acid, namely, when that acid is heated with hydriodic or hydrobromic acid (Kekulé, Ann. Ch. Pharm. Suppl. ii.



85); and, according to Mullhäuser (Ann. Ch. Pharm. ci. 171), is found among the products of the oxidation of protein-compounds by nitromuriatic acid.

Lassaigne, in 1819, first showed that in the dry distillation of malic acid, there is produced, besides maleic acid, another acid, which was further investigated by Pelouze in 1834, who called it paramaleic acid. Pfaff in 1826 found in Iceland moss (*Lichen islandicus*) an acid to which he gave the name of lichenic acid; and Winckler in 1833 obtained from fumitory (*Fumaria officinalis*) an acid designated as fumaric acid. The identity of this acid with paramaleic acid was demonstrated by Demarçay in 1834, and with lichenic acid by Schödler in 1836. The boletic acid found by Braconnot in *Boletus pseudo-ignarius*, and supposed by him to be a distinct acid, was shown by Bolley (Ann. Ch. Pharm. lxxxvi. 46) to be likewise identical with fumaric acid.

**Preparation.**—1. *From Fumitory.*—The aqueous decoction of the fresh flowering herb, together with the roots, after straining, subsidence, and decantation, is evaporated, first over the open fire and then over the water-bath, to a thin syrup; and this syrup, while still hot, is mixed with a small quantity of hydrochloric acid, and left for about a fortnight in a cool place, till the fumaric acid has separated in hard brown crystals. The mother-liquor is then diluted with water and poured off; the crystals washed with cold water, suspended in water, and slightly supersaturated with carbonate of potassium; the filtrate slightly supersaturated with sulphuric acid, heated in the water-bath, and filtered from the resulting dark brown resinous precipitate; the still brownish crystals of fumaric acid which form on cooling are dissolved in hot water; and the solution is digested with animal charcoal and filtered: it then, on cooling, yields snow-white crystals, amounting to 6.156 per cent. of the fresh herb (Winckler). The fumarate of calcium contained in the expressed juice may also be decomposed by oxalic acid. This salt is deposited spontaneously from the *Extractum Fumariae*, after two years' standing, in crystalline grains, which may be separated by diluting the extract with an equal quantity of cold water, then decanting and washing with cold water; when decomposed by aqueous oxalic acid, they yield a brownish acid, which may be freed from an admixed red-brown substance by mixing it with sand and subliming, or by solution in ether and filtration (Winckler, Répert. Pharm. xxxix. 48).—Trommsdorff (N. Tr. xxv. 2, 152) precipitates the recently expressed juice of fumitory—after separation of the scum which forms on boiling—with acetate of lead; decomposes the washed precipitate with sulphydric acid; and obtains, by evaporating and cooling the filtrate, brownish crystals which may be purified with animal charcoal. A similar process is followed by Demarçay. Delffs washes the yellowish green precipitate thrown down by acetate of lead (after it has somewhat diminished in volume by standing); dries it in the air on bibulous paper; rubs it to powder; stirs it up with nitric acid gradually added (whereupon the mass swells up, but gives off only a small quantity of nitrous vapours); agitates the resulting mixture of nitrate of lead and free fumaric acid, after 24 hours with a little water; filters; washes the residue with water; and extracts the fumaric acid with boiling alcohol of ordinary strength. The alcoholic solution is then evaporated; the residue dissolved in ammonia; the excess of ammonia expelled from the solution by heating; and a certain quantity of lead which remains in it, removed by sulphydric acid (the greater part of the colouring matter also separates with the sulphide of lead); the acid fumarate of ammonium is brought to the crystallising point; the crystals, if much coloured, are purified by pressure and recrystallisation; the salt is then dissolved in hot water; and the solution treated with nitric acid, to separate the fumaric acid, which then, after the liquid has cooled, crystallises out completely, but only after a considerable time. The nitric acid, if added in slight excess, generally effects the complete destruction of the colouring matter. By this process, Delffs obtained more than 5 drachms of pure fumaric acid from 20 lbs. of the herb.

2. *From Iceland Moss.*—Sixty-four pts. of the lichen are macerated for some time in water containing carbonate of potassium; the filtrate is precipitated with acetate of lead; the washed brownish precipitate decomposed by sulphydric acid; the filtrate evaporated; and the crystals of the acid, which still contain lime, are purified (Pfaff). The chopped lichen is macerated for six days with water and milk of lime, the mixture being frequently stirred; and the expressed turbid liquid is evaporated to half its bulk, acidulated with acetic acid, then heated, mixed with basic-acetate of lead, as long as reddish flocks containing brown colouring matter continue to separate, and filtered hot. The filtrate, on cooling, deposits white or brown-yellow needles of the lead-salt, and an additional quantity, though impure, on further evaporation; the lead-salt may be decomposed by sulphydric or sulphuric acid. The impure acid is purified by boiling with dilute nitric acid, and cooling to the crystallising point. (Schödler.)

3. *From Glaucium luteum.*—The expressed juice is boiled and precipitated by ammonia; the filtrate evaporated; mixed while still hot with a small quantity of nitric

acid; then with nitrate of lead; and left to cool till the lead-salt separates mostly in the crystalline form. (Probst, Ann. Ch. Pharm. xxxi. 248.)

4. *From Malic or from Maleic acid.*—Malic acid is heated for some time to a temperature a little above 130°, whereupon water passes over, together with maleic acid, and fumaric acid remains behind in the solid state; or, crystallised maleic acid is boiled in a long glass tube, so that the evolved water may continually flow back again, till the maleic is converted into fumaric acid (Pelouze). Dessaignes (Compt. rend. xlii. 524) obtains fumaric acid by heating malic acid for several hours with hydrochloric acid. On the other hand, fumaric acid is converted into malic acid by heating it with hydrochloric acid in sealed tubes. (See below.)

*Properties.*—The acid obtained from malic acid crystallises from the aqueous solution, in broad, striated, colourless prisms, sometimes rhombic, sometimes hexagonal (Pelouze); that obtained from fumitory, in scales united in stellate groups (Winckler); that from Iceland moss, in needles (Pfaff); in crystals aggregated in cauliflower-like tufts (Schödlér). The acid sublimes in long white needles (Lassaigne Winckler). It requires a high temperature to melt it; volatilises somewhat above 200° C. even before melting, and sublimes for the most part unaltered, but partly resolved into water and fumaric anhydride. It is inodorous, tastes very acid, and reddens litmus strongly (Winckler, Pelouze, and others). It dissolves sparingly in cold, readily in hot water; also in alcohol and ether.

*Decompositions.*—1. When fumaric acid is heated, a small portion of it is resolved into fumaric anhydride,  $C^4H^2O^3$ , which volatilises, and water (Pelouze).—2. It may be set on fire by a flaming body, and then burns with a pale blue flame (Winckler).—3. When triturated and heated with *peroxide of lead*, it first gives off water, and then takes fire, without emitting any odour of formic acid (Rieckher).—4. The colourless solution of the acid turns brown when heated (Winckler), and gives off sulphurous acid (Rieckher).—5. The aqueous solution of the acid is not altered by eight days' boiling, or when heated in a sealed glass tube to 250° C., not being in fact converted into malic acid. (R. Hagen.)

6. Fumaric acid enclosed with hydrochloric acid in a sealed tube, and heated to 100° C. for 140 hours, is partly converted into malic acid. On evaporating the resulting liquid to dryness, and treating the residue with a small quantity of water, to separate unaltered fumaric acid, the last mother-liquor yielded by evaporation a deliquescent syrup, which, after drying at 100° C., fused readily, and yielded fumaric acid by dry distillation. Another portion, half saturated with ammonia, yielded by evaporation, first crystals of acid fumarate of ammonium, which gave a precipitate with ferric chloride, then transparent prisms of a salt which did not precipitate ferric chloride, even after addition of ammonia, melted at 40° C. (acid fumarate of ammonium does not melt even at 200°), and was converted at 160° into fumarimide, which is the product obtained by heating acid malate of ammonium. Hence it appears that part of the fumaric acid treated as above described had been converted into malic acid. (Dessaignes, J. Pharm. [3] xxxii. 48.)

7. Fumaric acid is not decomposed by boiling with nitric acid, or with water and peroxide of lead, or acid chromate of potassium; and it does not precipitate platinum-black from solution of chloride of platinum: it exhibits therefore no great tendency to decompose under the influence of oxidising agents.—8. On the other hand, it easily takes up hydrogen, under the influence of certain reducing agents, and is converted into succinic acid:



This change takes place when aqueous fumaric acid is placed for a few hours in contact with *sodium-amalgam*, or when it is heated with *hydriodic acid*. In like manner, when heated to 120° C. in a sealed tube with *hydrobromic acid*, it is slowly transformed by addition of 1 at. HBr, into monobromosuccinic acid,  $C^4H^3BrO^4$ , and when heated for a few minutes to 100° in a sealed tube, with *bromine* and water, it is converted, by addition of 2 at. bromine, into dibromosuccinic acid,  $C^4H^2Br^2O^4$ . (Kekulé, Ann. Ch. Pharm. Suppl. i. 129; Rép. Chim. pure, 1861, p. 484; Jahresber. 1861, p. 365.)

**Fumarates.** Fumaric acid is dibasic, forming *dimetallic* or *neutral salts*,  $C^4H^2M^2O^4$ , and *monometallic* or *acid salts*,  $C^4H^3MO^4$ . Some of the fumarates are crystalline, others pulverulent, and most of them have a mild taste. None of them, excepting the ammonium, copper, and mercury salts, become carbonised till they are heated above 250° C. They are decomposed by phosphoric, sulphuric, hydrochloric, and nitric acids; but fumaric acid expels acetic acid from the acetates. Many fumarates dissolve in water, but none in strong alcohol. Solutions of the alkaline fumarates precipitate most metallic salts, but not those of zinc, aluminium, or chromium: fumarate of



zinc is easily soluble, and fumaric acid does not appear to be capable of forming salts with aluminium or chromium.

*Fumarates of Ammonium.*—The neutral salt is very soluble in water, and is converted into the acid salt by evaporation.

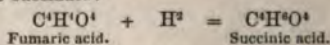
The acid salt is obtained by saturating fumaric acid with ammonia, and leaving the solution to evaporate in a non-exhausted receiver over lime and oil of vitriol, or in *vacuo* over hydrate of potassium. It crystallises in oblique rhombic prisms, truncated on the lateral edges, very soluble in water and alcohol. According to Pasteur (*Ann. Ch. Phys.* [3] **xxxi.** 91), the crystals are monoclinic prisms, usually exhibiting the faces  $\infty P$ ,  $\infty P\infty$ ,  $oP$ ,  $-P$ . Inclination of  $\infty P$  :  $\infty P$  in the orthodiagonal principal section =  $110^\circ$ ;  $oP$  :  $\infty P\infty$  =  $86^\circ 51'$ ;  $-P$  :  $-P$  =  $132^\circ 52'$ . The solution has no action on polarised light.

*Fumarate of Barium*,  $C^4H^2Ba^2O^4$  (at  $100^\circ C.$ ).—Fumaric acid does not precipitate baryta-water or chloride of barium. Fumarate of barium is obtained by dissolving fumaric acid in a hot solution of acetate of barium, or by mixing the two substances in hot concentrated solutions. It is then deposited on cooling in anhydrous crystalline grains. It may also be prepared by adding fumarate of potassium or ammonium to chloride of barium, being then deposited in small, shining, rhomboidal, hydrated prisms, which effloresce quickly in the air, giving off 15 per cent. water, and when heated to  $100^\circ C.$  lose 20.81 per cent. water. It is very soluble in water and alcohol, not soluble in fumaric acid, or in any other acids in the dilute state.

There does not appear to be an acid fumarate of barium.

*Fumarate of Calcium*,  $C^4H^2Ca^2O^4$  (at  $200^\circ C.$ ).—This salt occurs in fumitory. Fumaric acid does not precipitate lime-water (Lasaigne), or chloride of calcium. From a hot-filtered solution of carbonate of calcium in fumaric acid, or from a mixture of fumarate of potassium with acetate of calcium, colourless shining scales separate after a while, which are tasteless, permanent in the air, and scarcely soluble in water or alcohol. An aqueous mixture of fumaric acid and acetate of calcium deposits highly lustrous crystals, which are sparingly soluble in water, insoluble in alcohol, give off the greater part of their water at  $100^\circ C.$ , and the whole, amounting to 25.66 per cent. (3 at.) at  $200^\circ$ .

Fumarate of calcium, exposed for some weeks to the heat of summer, in contact with cheese, is converted into succinate:



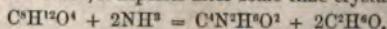
*Fumarate of Cobalt*,  $C^4H^2Co^2O^4 + 3 \text{ aq.}$ —A mixture of fumaric acid and acetate of cobalt does not yield crystals by evaporation; but on adding alcohol to the concentrated solution, fumarate of cobalt is deposited in the form of a rose-coloured pulverulent precipitate. It is very soluble in water and in ammonia, slightly in weak alcohol. It gives off 2 at. water at  $100^\circ C.$ , and 1 at. more at  $200^\circ$ , in all 3 at. = 23.82 per cent.

*Fumarate of Copper.*—Fumarate of potassium added to cupric sulphate, throws down a pale blue crystalline powder, soluble in hydrochloric or nitric acid, insoluble in water and alcohol. Aqueous cupric acetate, heated with fumaric acid till the latter dissolves, deposits a blue-green crystalline powder. This salt, after drying in the air, gives off 17.67 per cent. (rather more than 2 at.) water at  $100^\circ C.$ , and 23.61 (3 at.) in all at  $200^\circ$ ; at  $230^\circ$ , it suffers a total loss of 48 or 49 per cent., assuming at the same time a brown colour and being partially decomposed. It dissolves readily in nitric acid, with separation of fumaric acid; slowly in water and alcohol, and is insoluble in boiling fumaric acid. (Rieckher.)

*Fumarate of Cuprammonium* is deposited in shining dark blue octahedrons on evaporating a solution of fumarate of copper in ammonia. On adding alcohol to this solution, the salt is precipitated in silky blue needles.

*Fumarate of Ethyl*,  $C^4H^2(C^2H^5)^2O^4$ : *Fumaric ether*. Hagen (*Ann. Ch. Pharm.* **xxxviii.** 274).—A solution of fumaric or of malic acid in absolute alcohol is saturated with hydrochloric acid gas, the mixture distilled, and the fumaric ether, which passes over after the hydrochloric ether, and when the heat has risen considerably, is collected in a separate receiver, and dried over chloride of calcium. It is an oily liquid, heavier than water, and having a pleasant fruity odour; slightly soluble in water.

The ether heated with potash-ley, is resolved into fumarate of potassium and alcohol. Treated with aqueous ammonia, it deposits after some time crystals of fumaramide:



*Fumarate of Iron* (ferrie).—Recently precipitated ferrie hydrate does not dissolve in aqueous fumaric acid, even with the aid of heat. The aqueous acid forms a brownish yellow precipitate with ferrie sulphate. Fumarate of ammonium or sodium



forms with sesquichloride of iron a pale brown-red precipitate, insoluble in excess of the ammonia-salt (whereby it is distinguished from the precipitate formed by succinic acid). It is very bulky, and difficult to wash; soluble in acids but not in ammonia; and whether precipitated from cold or from hot solutions, contains after drying at  $200^{\circ}\text{C}$ . 44.08 per cent. ferric oxide.

*Fumarates of Lead.*—1. *Neutral or Diplumbic salt*,  $\text{C}^4\text{H}^2\text{Pb}^2\text{O}^4$  (at  $200^{\circ}\text{C}$ ).—Malate of lead is converted at  $200^{\circ}\text{C}$ . into fumarate (Rieckher). The dilute potassium-salt mixed with acetate of lead acidulated with acetic acid, throws down a white crystalline powder, which dissolves on boiling, and crystallises after a while, on cooling, in white shining tufts of needles. The free acid behaves in a similar manner with neutral acetate of lead. The dried salt does not decompose at  $200^{\circ}\text{C}$ . When heated over a flame, it takes fire and burns away with a glimmering light, leaving a mixture of lead and a small quantity of protoxide. The needles, after drying in the air, contain 16.28 per cent. (3 at.) water (Pelouze); 9.31 per cent. (2 at.) according to Rieckher. The salt dissolves readily in nitric acid, with separation of fumaric acid; it is nearly insoluble in cold water, and in strong acetic acid, but dissolves with tolerable facility in boiling water, separating out again unchanged on cooling. It is insoluble in alcohol.

2. A *sesplumbic salt*,  $\text{Pb}^3\text{O}^4\cdot 2\text{C}^4\text{H}^2\text{Pb}^3\text{O}^4$  (at  $230^{\circ}\text{C}$ .), is obtained by precipitating basic acetate of lead with acid fumarate of potassium. The white precipitate, which quickly sinks down, gives off all its water of crystallisation at  $130^{\circ}\text{C}$ ., and bears a temperature of  $230^{\circ}$  without decomposition. (Rieckher.)

3. Another *sesplumbic salt*,  $2\text{Pb}^3\text{O}^4\cdot \text{C}^4\text{H}^2\text{Pb}^3\text{O}^4$  (at  $230^{\circ}\text{C}$ .), is obtained by treating the neutral salt with ammonia. (Rieckher.)

*Fumarate of Magnesium*,  $\text{C}^4\text{H}^2\text{Mg}^2\text{O}^4$  (at  $200^{\circ}\text{C}$ .).—Fumaric acid mixed with aqueous acetate of magnesium, and evaporated to a syrup, yields no crystals; but if the greater part of the acetic acid be expelled by thorough drying in the water-bath, and the residue exhausted with alcohol, fumarate of magnesium remains undissolved, in the form of a white powder, which gives off 34.48 per cent. (4 at.) water at  $200^{\circ}\text{C}$ ., but only 2 at. at  $100^{\circ}$ .

*Fumarate of Manganese*,  $\text{C}^4\text{H}^2\text{Mn}^2\text{O}^4 + 3\text{aq}$ .—Fumarate of ammonium added to a solution of manganous sulphate precipitates this salt in the form of a white powder. When fumaric acid is heated with solution of manganous acetate, a white powder is formed, containing 3 at. = 24.7 per cent. water, which it gives off at  $100^{\circ}\text{C}$ . The salt is sparingly soluble in water, insoluble in alcohol.

*Fumarates of Mercury.*—1. *Mercuric salt*.—The potassium-salt throws down from the solution of mercuric chloride, a mixture of yellow needles and a white crystalline salt. Free fumaric acid gives no precipitate, either with corrosive sublimate or with mercuric nitrate; it does not dissolve mercuric oxide, even with the aid of heat. (Rieckher.)

*Mercurous salt*.—An aqueous solution of mercurous nitrate forms with fumaric acid or alkaline fumarates, a white crystalline precipitate, which suffers no perceptible loss and no change of colour at  $100^{\circ}\text{C}$ . (Rieckher.)

*Fumarate of Nickel*.—Obtained like the cobalt-salt. Pale green powder, which, after drying in the air, gives off 26.49 per cent. (rather more than 3 at.) water, 30.61 per cent. (4 at.) in all at  $200^{\circ}\text{C}$ ., and at  $230^{\circ}$  suffers a total loss of 36.22 per cent. with colouring and partial decomposition. It dissolves in water, weak alcohol, and ammonia. (Rieckher.)

*Fumarates of Potassium.*—1. The *neutral salt*,  $\text{C}^4\text{H}^2\text{K}^2\text{O}^4 + 2\text{aq}$ ., obtained by neutralising the acid with aqueous carbonate of potassium, and evaporating, forms large, transparent, colourless rhombic tables and four-sided prisms, often aggregated in stars, permanent in the air, and having a mild, scarcely saline taste (Winckler); or laminae united in radiating groups (Pelouze). The salt effloresces during the evaporation of its solution, but deposits shining striated prisms at the bottom of the vessel; sometimes the solution yields on evaporation a liquid which, in 12 to 24 hours, is converted into a crystalline powder. The crystals become opaque at a gentle heat, and give off 17.06 per cent. (4 at.) water at  $100^{\circ}\text{C}$ .; at a higher temperature, they melt imperfectly, blacken, swell up to ten times their original bulk, and leave a residue of charcoal and carbonate of potassium. The salt dissolves readily in water, but not in alcohol (Rieckher). From a concentrated aqueous solution, acetic acid throws down the acid potassium-salt; alcohol, the neutral salt, containing 16.61 per cent. (therefore 2 at.) water of crystallisation.

2. *Acid salt*,  $\text{C}^4\text{H}^3\text{K}^2\text{O}^4$ .—From the cold-saturated aqueous solution of the neutral salt, water saturated with fumaric acid precipitates the acid salt in needles. It forms shining, tufted needles, and oblique four-sided prisms, permanent in the air, and having a pleasant, strongly sour taste. They give off 1 at. water at  $200^{\circ}\text{C}$ ., and decompose at a higher temperature, like the neutral salt. They dissolve much less abundantly in cold water than the neutral salt, plentifully in boiling water; are nearly

insoluble in cold alcohol of 81 per cent., but dissolve sparingly therein at a boiling heat, and crystallise on cooling.

**Fumarate of Silver**,  $C^4H^2Ag^2O^4$ .—Free fumaric acid added to nitrate of silver throws down a fine white powder (Lassaigne). The acid, even when dissolved in 200,000 pts. of water, still precipitates silver-solution; and alkaline fumarates precipitate it even at higher degrees of dilution, so completely, indeed, that the filtrate shows no turbidity on the addition of hydrochloric acid (Pelouze). The powder, after being washed and dried in the dark, is white, tolerably heavy, nearly tasteless, and adheres to the fingers. It turns brown when heated, afterwards decomposes, with slight detonation and sparkling, and leaves a bulky, velvet-black mass, which leaves metallic silver when burnt. When heated, it deflagrates like gunpowder. It dissolves readily in nitric acid, with liberation of fumaric acid. It is insoluble in water, and is not decomposed by continued boiling. It dissolves readily in ammonia, and when the ammonia evaporates, yields delicate shining prisms, which give off potash when treated with ammonia.

**Fumarate of Sodium**,  $C^4H^2Na^2O^4$ .—The salt precipitated by alcohol from the aqueous solution, is a crystalline powder containing 10.03 per cent. (1 at.) water; when the solution is evaporated, the salt crystallises in needles and prisms containing 25.12 per cent. (3 at.) water. The water escapes, for the most part, at  $100^\circ C.$ , completely at  $200^\circ$ , and the residue contains 38.77 per cent. soda. It is a crystalline mass consisting of needles, permanent in the air, having a faint silky lustre, and a warm saline taste; it behaves in the fire like the potassium-salt, dissolves readily in cold water, but is insoluble in alcohol.

It does not appear possible to prepare an acid fumarate of sodium or a fumarate of sodium and potassium, or of ammonium and potassium. (Rieckher.)

**Fumarate of Strontium**,  $C^4H^2Sr^2O^4 + 3 \text{ aq.}$ .—Aqueous fumaric acid does not precipitate strontia-water; but on adding the acid to a solution of acetate of strontium, a white crystalline powder is precipitated, consisting of fumarate of strontium with 3 at. water. It is very slightly soluble in water and in alcohol.

**Fumarate of Zinc**,  $C^4H^2Zn^2O^4 + 3 \text{ aq.}$ .—Aqueous fumaric acid, saturated at the boiling heat with oxide or carbonate of zinc, yields, on further concentration, large oblique prisms having a vitreous lustre; very soluble in water, but insoluble in alcohol, and containing 3 at. crystallisation-water; but the same solution, if left to evaporate spontaneously in a cool place, yields crystals which contain 4 at. water (29.06 per cent.) and effloresce in the air.

**FUMARIC ANHYDRIDE**,  $C^4H^2O^3 = (C^4H^2O^3)^{\cdot}O$ . (Pelouze, Ann. Ch. Phys. [2] lvi, 72.)—This body, which may also be regarded as maleic anhydride, is produced when maleic or fumaric acid is heated. To prepare it, crystallised maleic acid is rapidly distilled, with change of receiver, till nothing but crystallised fumaric acid remains behind; and the last distillate (the first being watery) is repeatedly rectified in the same manner, the first watery portion of the distillate being each time set aside, till the last distillate passes over completely, without first yielding water, and without leaving a residue of fumaric acid.

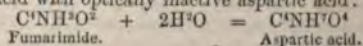
The anhydride melts at  $57^\circ C.$ , and boils at  $176^\circ$ . When slightly heated above its boiling point, it decomposes, turning brown, and giving off gas.

**FUMARIC ETHER**. See FUMARATE OF ETHYL (p. 744).

**FUMARIMIDE**,  $C^4NH^2O^2 = N \begin{Bmatrix} C^4H^2O^3 \\ H \end{Bmatrix}$ . (Dessaigues, Compt. rend.

xxx. 324; J. Wolff, Ann. Ch. Pharm. lxxv. 293.)—Formed by the action of heat on acid malate of ammonium. When this salt is heated in an oil-bath to  $160^\circ$ – $200^\circ C.$ , it melts, swells up, gives off water containing a very small quantity of ammonia, and leaves a reddish, transparent, somewhat resinous mass, very sparingly soluble in water, even at the boiling heat. This residue, after being washed with hot water, forms an amorphous powder, having a pale brick-red colour and earthy taste. When dried at  $100^\circ$ , it exhibits the composition of fumarimide +  $\frac{1}{2}$  at. water (Dessaigues). When the residue obtained as above is exhausted with boiling water, the wash-water yields on cooling, a fine white powder, which remains suspended in the liquid, but is immediately precipitated by acids. This substance, after being several times dissolved in water and reprecipitated, exhibits nearly the composition of anhydrous fumarimide. (Wolff.)

Fumarimide is a very stable substance. It dissolves in hot concentrated acids, whence it is precipitated by water without alteration, even after boiling for some seconds. But if heated for five or six hours with hydrochloric or nitric acid, and then evaporated to dryness, it yields a crystalline residue containing a compound of hydrochloric or nitric acid with optically inactive aspartic acid:



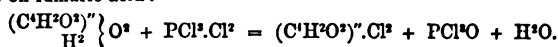
Acid maleate and acid fumarate of ammonium yield, by dry distillation, a substance closely resembling fumarimide in most of its reactions, but not identical with it. (Dessaignes.)

**FUMARINE.** An organic base, contained in fumitory (*Fumaria officinalis*), first observed by Peschier (*Liebig's Organische Chemie*, p. 633); more fully examined by Hannon (*J. Chim. méd.* [3] viii. 705). The plant grown on a well-manured soil, and gathered in June or July while in full flower, contains from 5 to 6 per cent. of this base, to which it appears to owe its specific physiological action. To obtain it, the plant is beaten up to a pulp with an equal weight of water, the pulp acidulated with acetic or hydrochloric acid, then heated for some hours over the water-bath, and filtered. The filtrate evaporated to a syrup is treated with boiling alcohol, which dissolves the acetate or hydrochlorate of fumarine, and, after concentration and decolorisation with animal charcoal, deposits it in slender needles. Or the expressed and filtered juice of the plant is mixed with twice its bulk of water, and precipitated with basic acetate of lead, the excess of lead is removed from the filtrate with dilute sulphuric acid, and the liquid is evaporated; it then deposits crystalline sulphate of fumarine. (Hannon.)

Fumarine is separated from its salts by caustic alkalis or their carbonates, in the form of a curdy precipitate. It may be obtained in the crystalline form by spontaneous evaporation of its hot alcoholic solution, but not by evaporation with the aid of heat. The salts have a bitter taste. (Hannon.)

**FUMAROLES.** See VOLCANIC EMANATIONS.

**FUMARYL CHLORIDE OF.**  $C^4H^2O^2.Cl^2$ . (Kekulé, *Ann. Ch. Pharm. Suppl.* ii. 85; *Rép. Chim. pure*, 1863, p. 31.)—Produced by the action of perchloride of phosphorus on fumaric acid:



When purified, it boils at  $160^\circ C$ . It unites directly with 2 at. bromine and is converted into chloride of dibromosuccinyl,  $C^4H^2Br^2O^2.Cl^2$ .

**FUMIGATION.** See the article DISINFECTANT in *Ure's Dictionary of Arts, Manufactures, and Mines*, ii. 27.

**FUMING LIQUOR OF BOYLE.** A mixture of two or more sulphides of ammonium, obtained by distilling sulphur with sal-ammoniac and quick lime (i. 194).

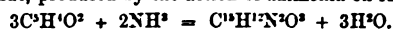
**FUMING LIQUOR OF CADET.** A mixture of cacodyl and oxide of cacodyl, obtained by distilling acetate of potassium with arsenious anhydride (i. 403).

**FUMING LIQUOR OF LIBAVIUS.** Tetrachloride of tin.

**FUNGIC ACID.** The name given by Braconnot to an acid which he found to exist in a considerable number of agarics (*Ann. Chim.* lxxix. 265; *Ann. Ch. Phys.* xxx. 272). According to Dessaignes, however (*Compt. rend.* xxxvii. 782), the acid in question is nothing but a mixture of citric, malic, and phosphoric acids.

**FUNKITE.** A green coccolite.

**FURFURAMIDE.**  $C^5H^7N^1O^2 = N^2 \left\{ \begin{array}{c} C^5H^5N^1O^2 \\ H^2 \end{array} \right\}$ . (Fownes, *Phil. Trans.* 1845, 253.)—An amide, produced by the action of ammonia on furfural:



Furfural set aside with five times its volume of aqueous ammonia, is converted, partially in a few hours, and completely after a longer time, into a yellowish-white, bulky, crystalline mass of furfuramide. A mixture of aqueous furfural and ammonia yields the same compound, in a few days, purer and whiter. The resulting yellowish-white mass may be dissolved in hot alcohol, and crystallises therefrom on cooling in short needles united in tufts.

Furfuramide is fusible, nearly inodorous when dry, insoluble in cold water, but easily soluble in alcohol and ether. It burns with a smoky flame and leaves a small quantity of charcoal. When exposed to damp air, or heated with water or alcohol, it is slowly resolved into ammonia and furfural; acids produce this decomposition instantly. Furfuramide boiled with dilute potash-ley, is converted, without the slightest evolution of ammonia, into furfurine (Fownes). Furfuramide treated with sulphuric acid yields thiofurfal. (Cahours.)

**FURFURINE.**  $C^5H^7N^1O^1$ . (Fownes, *Phil. Trans.* 1845, 253; Stenhouse, *Ann. Ch. Pharm.* lxxiv. 289; Stanberg and Bergstrand, *J. pr. Chem.* lxxi. 239.)—An organic base, isomeric with furfuramide, and produced therefrom under the influence of caustic potash, or simply of heat.

*Preparation.*—1. Dried furfuramide is added to a large quantity of dilute boiling potash-ley; the liquid left to cool slowly after ten or fifteen minutes, whereupon the furfurine



which has separated in the form of a yellowish oil, solidifies, and the portion remaining in solution crystallises out; the whole of the furfurine is collected on a filter, washed with cold water, and dissolved in excess of boiling aqueous oxalic acid, from which impure acid oxalate of furfurine crystallises on cooling; this impure oxalate is washed on a filter with cold water, and dissolved in boiling water; the solution boiled for a few minutes with animal charcoal previously purified by hydrochloric acid, then filtered at the boiling heat; the pure white salt which separates on cooling is dissolved in boiling water, the solution supersaturated with ammonia, and filtered hot; and the crystals of furfurine, which form on cooling, are washed with cold water (Fownes). The crude base may also be purified by repeated solution in alcohol and precipitation with water (Svanberg and Bergstrand).—2. Furfuramide is also readily converted into furfurine by heating it for half an hour to  $110^{\circ}$ – $120^{\circ}$  C. The resulting brown mass dissolved in alcohol, and treated with excess of oxalic acid, yields acid oxalate of furfurine, from which the base may be obtained as above. By this means furfurine may be prepared directly from furfural, viz. by passing dry ammoniacal gas into furfural heated to  $110^{\circ}$ – $120^{\circ}$  C. The furfural then turns brown, and in the course of half an hour to an hour, is converted into furfurine. (C. Bertagnini, *Ann. Ch. Pharm.* lxxxviii. 128.)

**Properties.**—Furfurine crystallises in white, soft, silky needles, resembling those of caffeine. It melts considerably below  $100^{\circ}$  C., to a nearly colourless oil, which, on cooling, solidifies to a soft resin, and afterwards to a resinous crystalline mass. It is permanent in the air (Fownes). When perfectly dry, it remains unaltered on exposure to the air; but when moist, it quickly turns greyish-green, yellowish-brown, and often red (Svanberg and Bergstrand). It is inodorous, and has but little taste. It exhibits an alkaline reaction, which is particularly strong in the hot aqueous or alcoholic solution (Fownes). When a tolerably strong solution of neutral sulphate of furfurine is heated, the precipitated brown powder (p. 749) separated by filtration, and the filtrate treated with ammonia, furfurine is precipitated, not in the pulverulent or crystalline state, but in the form of a tough coherent mass, which, after a little kneading, becomes brittle and as hard as stone; the recently precipitated mass, when examined by the microscope, exhibits here and there crystalline groups like snow-flakes. Furfurine appears then, when heated, to pass, like quinine, into another modification (Svanberg and Bergstrand). It dissolves in 1.57 pts. of boiling water, and separates almost completely on cooling; readily in cold alcohol or ether, and crystallises when the solvent is evaporated. (Fownes.)

Furfurine, when heated in the air, burns with a red smoky flame, and leaves a trace of charcoal (Fownes). Aqueous periodic acid decomposes it, with separation of iodine. (Bödeker, *Ann. Ch. Pharm.* lxxi. 64.)

**Furfurine-salts.** Furfurine dissolves very readily in dilute acids and neutralises them completely. It expels ammonia from sal-ammoniac at a boiling heat, but at ordinary temperatures is itself precipitated from its combinations with acids, by ammonia, potash, or soda. The salts of furfurine have an extremely bitter taste. They are precipitated white by corrosive sublimate, yellow by dichloride of platinum, but give no precipitate with tincture of galls. (Fownes.)

**Acetate of Furfurine** is very soluble in water, and very difficult to crystallise.

**Carbonate.** (?)—According to Döbereiner, furfurine unites with carbonic acid. According to Davidson, on the contrary, the base dissolves in water through which carbonic acid is passed, but separates out unaltered when the solution is left to evaporate.

**Chromate (acid),**  $2C^3H^3N^2O^3.H^2O.2Cr^2O^3$ .—Orange-yellow powder, sparingly soluble in cold water, becoming brown when dry. (R. Davidson, *Ed. N. Phil. J.*, new series, ii. 284.)

**Hydrobromate,**  $C^3H^3N^2O^3.HBr$  + aq.—Short prismatic needles soluble in 26 pts. water. (Davidson.)

**Hydrochlorate,**  $C^3H^3N^2O^3.HCl$  + aq.—Dilute hydrochloric acid saturated with furfurine, yields tufts of delicate, silky, neutral needles, which retain their lustre when dried in vacuo over sulphuric acid. They dissolve readily in water, less easily in hydrochloric acid. (Fownes.)

The **chloroplatinat**e,  $C^3H^3N^2O^3.HCl.PtCl_2$ , is obtained as a light-yellow precipitate, on mixing the solution of the hydrochlorate with excess of chloride of platinum (Fownes). When the chloride of platinum is poured into a hot solution of hydrochlorate of furfurine in weak alcohol, the platinum-salt of furfurine separates on cooling in long light yellow needles resembling picrate of potassium. (Stenhouse.)

Hydrochlorate of furfurine also forms double salts with *mercuric chloride* (Fownes), and with the *chlorides of gold, palladium and iridium*. (Döbereiner.)

**Hydriodate,**  $C^3H^3N^2O^3.HI$  + aq.—Colourless, slender, oblique four-sided prisms, soluble in 55 pts. of cold water; soluble also in alcohol and ether. (Davidson.)

**Mellate.**—Aqueous mellic acid neutralised with furfurine yields the salt, after a while, in nodular groups of crystals, which by recrystallisation are obtained in beautiful monoclinic prisms. The salt gives off 5.7 per cent. water between 100° and 125° C., and begins to turn yellow at 130°. (Karmrodt, *Ann. Ch. Pharm.* lxxi. 171.)

**Nitrate,**  $C^4H^4N^2O^4.HNO^3$ .—Transparent, colourless, highly lustrous, hard crystals, which effloresce in vacuo over sulphuric acid, and dissolve readily in water, slowly in nitric acid. (Fownes). According to Stenhouse, it crystallises from the aqueous solution in long irregular acuminate crystals; but from the alcoholic solution, in very regular rhombic prisms of considerable size and peculiar lustre; if, however, very strong alcohol is used, the crystals, which are at first perfectly transparent, soon become opaque, whereas those obtained from weak alcohol retain their lustre and transparency.

**Oxalates.**—The neutral oxalate forms tufts of needles very soluble in water. The acid oxalate forms thin transparent tables, which retain their lustre in a dry vacuum, redden litmus strongly, and dissolve very sparingly in cold, more readily in warm water. (Fownes.)

**Perchlorate,**  $C^4H^4N^2O^4.HClO^4 + aq.$ —Furfurine dissolved in warm very dilute perchloric acid, yields very long, thin, brittle prisms, having a glassy lustre and a disagreeable, saline, bitter taste; they effloresce at 60° C., melt at 160° to 160°, solidifying on cooling to a glassy brittle mass, and explode at a higher temperature. They dissolve readily in water and alcohol (Bödeker, *Ann. Pharm.* lxxi. 63). The crystals are right rhombic prisms, having the angles of the lateral edges = 72° 33' and 107° 27', the obtuse lateral edges truncated, the acute bevelled; cleavage from one obtuse lateral edge to the other. (Dauber, *Ann. Ch. Pharm.* lxxi. 67.)

**Phosphates of Furfurine.**—*a. Metaphosphate (?)*—When strongly ignited ammonio-sodic phosphate was dissolved in water, the solution precipitated by chloride of barium, and the washed metaphosphate of barium digested for 24 hours with neutral sulphate of furfurine, a filtrate was obtained which had a neutral reaction, but did not yield any crystallisable compound. On evaporation, it left a gummy mass, which became black and glassy when heated. (Svanberg and Bergstrand.)

*b. Orthophosphates.*—*a.*  $C^4H^4N^2O^4.H^3PO^4$ .—A boiling alcoholic solution of furfurine, mixed with a large excess of ordinary phosphoric acid, deposits crystals on cooling, which gradually assume a brownish yellow colour, if left in the mother-liquor; but if quickly taken out, and pressed between paper, retain their silvery lustre on subsequent exposure to the air. They are right four-sided prisms, so short that they appear like thin laminae. The crystals do not diminish in weight or decompose at 160° C., but when more strongly heated, they assume a blackish grey colour, and between 200° and 215° melt into a black vitreous mass, which dissolves completely in warm alcohol, and then no longer exhibits the reactions of ordinary phosphoric acid. The salt dissolves sparingly in cold, readily in hot water and alcohol, but appears to be insoluble in ether. (Svanberg and Bergstrand.)

*β.*  $(C^4H^4N^2O^4)^2.H^3PO^4$ .—Obtained by adding 1 at. furfurine dissolved in alcohol to a solution of 1 at. of the salt *a*, and heating the mixture. The filtrate on cooling deposits white, shining, oblique, four-sided, anhydrous prisms, which in the dry state are permanent in the air. They may be heated to 130°—135° C. without decomposition, but at higher temperatures behave like the salt *a*. The neutral salt dissolves readily in boiling water and alcohol, but is nearly insoluble in ether. (Svanberg and Bergstrand.)

*γ.*  $(C^4H^4N^2O^4)^3.H^3PO^4$ .—A solution of the salt *a* mixed with a large excess of the alcoholic solution of furfurine, deposits this salt on cooling in long oblique four-sided prisms, which are white and destitute of lustre; anhydrous; permanent in the air; may be heated to 120°—135° C. without decomposition; but at higher temperatures, behave like the two preceding salts. They dissolve readily in water and alcohol, but very sparingly in ether. The solutions have an alkaline reaction. (Svanberg and Bergstrand.)

*c. Pyrophosphate,*  $(C^4H^4N^2O^4)^4.H^4P^2O^7 + aq.$ —An alcoholic solution of furfurine, neutralised with pyrophosphoric acid, and evaporated in the drying chamber, ultimately yields a glassy crystalline crust, which dissolves readily in water and alcohol, and has a neutral reaction. The salt gives off 1.5 per cent. water at ordinary temperatures, and 2.14 per cent. more at 100° C. Hence if the 1.5 per cent. be regarded as hygroscopic, the salt may be supposed to contain 1 at. water. Between 115° and 120°, it assumes a greyish aspect, apparently from incipient decomposition. (Svanberg and Bergstrand.)

**Sulphate of Furfurine.**—*a. Neutral.*—Sulphuric acid saturated with furfurine, deposits when evaporated, either by heat or under the exsiccator, a black-brown powder.



When hydrochlorate of furfarine is decomposed with sulphate of silver, the crystals are deposited from the coloured and acid mother-liquor, but they contain only 0.3 per cent sulphuric acid, and therefore cannot consist of sulphate of furfarine.

*b. Acid salt*,  $C^5H^4N^2O^3.H^2SO^4 + 3\frac{1}{2} aq.$ —When furfarine is dissolved in somewhat dilute sulphuric acid, and a slight excess of the acid added after the solution has been warmed, short four-sided prisms are soon deposited (irregular rhombic tablets, according to Davidson), which dissolve readily in water, less readily in alcohol or ether, and least of all in water acidulated with sulphuric acid. The solution has a sour and bitter taste, and is coloured red by strong sulphuric acid. The salt effervesces readily at ordinary temperatures, giving off all its water of crystallisation, amounting to 21.62 per cent. ( $3\frac{1}{2}$  at.). Between  $80^\circ$  and  $90^\circ$  C., it loses  $\frac{1}{2}$  of its weight, and appears to decompose; at a higher temperature, it cakes together, and then melts into a black mass, which no longer dissolves completely in water. (Svanberg and Bergstrand.)

*Tartrate of Furfurine (acid)*.—This salt crystallises from a rather acid solution of furfarine in tartaric acid, in oblique four-sided prisms, which are permanent in the air, and do not give off water at  $150^\circ$  C. When treated with potash, they give off ammonia. The solution mixed with ammonia does not yield any precipitate of furfarine (Svanberg and Bergstrand.)

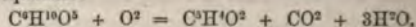
*Ethyl-furfurine*.  $C^5H^4N^2O^3 = C^5H^4(C^2H^5)N^2O^3$ .—The hydriodate of this base is obtained by heating alcoholic furfarine with iodide of ethyl to  $100^\circ$  C. in a sealed tube. It separates from a hot alcoholic solution as a gummy mass, but by spontaneous evaporation it may be obtained in fine crystals derived from a rhombic prism. It dissolves in 36 pts. of water, and more freely in alcohol and ether. (Davidson, *loc. cit.*)

*Hydrate of Ethyl-furfurine*,  $C^5H^4N^2O^3.HO$ , according to Davidson, more probably  $C^5H^4N^2O^3.2HO$ . or  $\begin{matrix} C^5H^4N^2O^3 \\ H \end{matrix} O$ , is obtained by decomposing the hydriodate with moist oxide of silver, and evaporating the filtrate. It is syrupy, easily soluble in alcohol, sparingly in water, and expels ammonia from its salts at  $100^\circ$  C. The chloroplatinate has the composition  $C^5H^4N^2O^3.HCLPtCl^2$ .

It does not appear possible to replace another atom of hydrogen in furfarine by ethyl or other alcohol-radicle.

*Amyl-furfurine*.  $C^5H^4N^2O^3 = C^5H^4(C^4H^9)N^2O^3$ .—The hydriodate, obtained by heating furfarine with iodide of amyl for four days, is a gummy mass, which dissolves but sparingly in water, but may be obtained in radio-crystalline masses. The chloroplatinate,  $C^5H^4N^2O^3.HCLPtCl^2$ , is a yellow powder sparingly soluble in water. (Davidson.)

**FURFUROL**.  $C^5H^4O^2$ . (Döbereiner [1831], Schw. J. lxxiii. 268.—Ann. Ch. Pharm. iii. 141.—Stenhouse, Phil. Mag. [3] xviii. 122; xxxvii. 226.—Fownes, Phil. Trans. 1845, 253; Ann. Ch. Pharm. liv. 52; Pharm. J. Trans. viii. 113.—Cahours, Ann. Ch. Phys. [3] xxiv. 277.—Schwanert, Ann. Ch. Pharm. cxvi. 257.)—A volatile aromatic oil which may be regarded as the aldehyde of pyromucic acid ( $C^5H^4O^3$ ), being convertible into that acid by oxidation: isomeric with fucosol (p. 718). It is produced by heating sugar, starch, bran, madder, and other vegetable substances with dilute sulphuric acid, either alone or mixed with peroxide of manganese, and appears to be a product of oxidation; thus, its formation from starch might be represented by the equation:



Döbereiner, who first obtained it as a secondary-product in preparing formic acid by distilling sugar with sulphuric acid and peroxide of manganese, called it *Artificial oil of Ants* (*künstliches Ameisenöl*). The name furfural is derived from *furfur* (bran) and *oleum* (oil).

From the experiments of Döbereiner and of Cahours, it would appear that sugar, starch, and sawdust distilled with sulphuric acid alone, do not yield furfural. According to Stenhouse, on the other hand, chips or shavings distilled with dilute sulphuric acid, yield furfural: also linseed-cake, the woody shell of the cocoa-nut, and mahogany. The furfural obtained from mahogany is very free from resin, and more easily purified than that obtained from other sources. According to Emmet (Sill. Am. J. xxxii. 140), sugar, starch, gum, and wood, distilled with sulphuric acid, so far diluted as not to exert any carbonising action, yields at  $100^\circ$  C. scarcely anything but furfural; but as soon as the residue blackens, nothing but formic acid is obtained. Fownes obtained only indistinct indications of furfural by distilling starch with dilute sulphuric acid, and from recently washed linen, not a trace. He is of opinion that the source of the furfural is to be found in the matter which lines the interior of the vegetable cells, called by Payen, *matière incrustante*. Furfural is likewise obtained by heating bran



with a very strong solution of chloride of zinc. The greater the quantity of starch in the bran, the smaller is the quantity of furfural obtained. Pure starch and pectin distilled with chloride of zinc, do not yield furfural. Bran distilled with chloride of calcium does not yield furfural, but possibly might do so if heated under pressure (Babo, *Ann. Ch. Pharm.* lxxxv. 100). Furfural is also found among the products of the dry distillation of sugar. (Völckel, *ibid.* 59.)

*Preparation.*—1. One part of sugar is distilled with 3 pts. of manganese, 3 pts. of oil of vitriol, and 5 pts. of water; the formic acid in the distillate saturated with carbonate of sodium; the liquid redistilled; the distillate saturated with chloride of calcium; and lastly, the furfural distilled off (Döbereiner).—2. One part of wheat-flour or saw-dust is distilled with 1 pt. of oil of vitriol diluted with an equal bulk of water in a copper still, which may be half filled with the mixture, the distillation being continued till the residue begins to char; the distillate, together with about as much water as was at first used, poured back into the still; the liquid redistilled nearly to dryness; the formic and sulphurous acids in the distillate—which is rendered milky by the furfural—saturated with potash, which colours the liquid yellow; one-fourth of the liquid then distilled off; the resulting distillate mixed with a large quantity of chloride of calcium and partially distilled; and this process repeated, if necessary, till the greater part of the oil, which is surmounted by an aqueous solution of itself—is obtained in the free state. By this process, 100 pts. of flour yield 0.52 pts. of furfural (Stenhouse).—3. Two parts of oatmeal are heated with 2 pts. of water and 1 pt. of oil of vitriol in a still, and the mixture stirred, till the pasty mass has become liquid from formation of dextrin; the liquid is then distilled; 1 pt. more of water added as soon as sulphurous acid begins to escape; the distillation continued till sulphurous acid comes off in larger quantity; the whole distillate poured back into the still; half of it poured off; and this half neutralised, as in 2, with potash, &c. (Fownes).—4. Two pts. of bran are distilled in a similar manner with 2 pts. of oil of vitriol and 6 pts. of water; by this process, 100 pts. of bran yield 0.8 pts. of furfural (Fownes). In subsequent experiments, Fownes obtained, by distilling 64 oz. (troy) of wheat-bran with 32 oz. sulphuric acid and an equal volume of water, 1 oz. of furfural; and from 64 oz. wheat flour, treated in the same manner, about 1½ drms. of impure furfural.—5. Six pts. of bran are distilled with 5 pts. of oil of vitriol and 12 pts. of water in a capacious still, till a strong odour of sulphurous acid is emitted, and the distillate is partially and repeatedly rectified over chloride of calcium. One hundred parts of bran yield by this process 2.6 pts. of furfural in all, part of which is held in solution in the watery distillate, but may be precipitated by ammonia in the form of furfamide (Gahours).—6. To save the repeated rectifications, the first distillate may be immediately saturated with ammonia; the mixture set aside for 24 hours in a cool place, and shaken occasionally; the furfamide which separates is then to be distilled with dilute hydrochloric acid not in excess, and the distillate rectified over chloride of calcium (Döbereiner).—7. According to Stenhouse, a very advantageous process for preparing furfural is to distil bran with more than half its weight of sulphuric acid previously diluted with 2 pts. of water. Hydrochloric acid may also be used, but it has the disadvantage of distilling over with the oil. To obtain furfural in large quantity, Stenhouse mixes 32 lbs. of wheat-bran with 20 lbs. of sulphuric acid, diluted as just mentioned, in a capacious three-necked glazed earthenware Woulfe's bottle (such as are used in the preparation of nitric and hydrochloric acids on the large scale); distils by passing steam into the mixture; neutralises the strongly acid distillate with chalk; rectifies the distillate repeatedly; and separates the oil by saturating the liquid with common salt and redistilling: this process yields from 12 to 13 ounces of crude furfural, containing a considerable quantity of acetone. Schwanert proceeds in a similar manner, using 100 pts. strong sulphuric acid and 300 pts. water to 100 pts. bran, and obtains 3 pts. of furfural, partly directly, partly after conversion into furfamide by ammonia and subsequent decomposition of that compound by distillation with hydrochloric acid.—8. Bran and chloride of zinc (in the proportion of 3 to 2½ : 1), in the state of solution, strong enough to form a damp mass cohering in lumps, are distilled together, whereupon water passes over first, then furfural, then hydrochloric acid, and lastly a solid fatty mass consisting of margaric acid with a small quantity of a hydrocarbon. The distillate is strained through linen, neutralised with potash, saturated with common salt, and rectified; and the furfural, after being separated from the water which passes over with it, is dried over chloride of calcium and again rectified. The watery portion of the distillate still contains a little furfural, which may be converted into furfamide as in (6). Six pounds of bran thus treated yielded from 1 to 2 oz. and sometimes more of furfural; bran containing a larger proportion of starch yielded less (Babo, *Ann. Ch. Pharm.* lxxxv. 100).—9. The most abundant and economical source of furfural is in the preparation of garancin by boiling madder with sulphuric acid. If the wooden boilers in which garancin is

usually manufactured were fitted with condensers, furfural might be obtained in any quantity without expense. Furfural is also produced by boiling any kind of madder with solution of sulphate of aluminium. (Stenhouse, *Epistolary communication*.)

Crude furfural obtained from any of the preceding sources is always contaminated with another aromatic oil, *metafurfural*, which has a higher boiling point; oxidises very readily; is for the most part converted during the distillation into a brown resin, and when mixed with a few drops of strong sulphuric, hydrochloric, or nitric acid immediately exhibits a purple colour, a reaction formerly indicated by Stenhouse and Fownes as characteristic of furfural; pure furfural does not exhibit it. Furfural may be freed from metafurfural by repeated rectification; the latter, being less volatile and much more oxidable, remains behind. The purity of the product may be tested by boiling an aqueous solution of the furfural for a few minutes with caustic potash, and treating the dark yellow liquid with excess of sulphuric or hydrochloric acid; if metafurfural is present, a deep red colour is produced; if not, the colour remains unchanged. (Stenhouse.)

*Properties.*—Furfural when recently prepared is a colourless oil, but it soon turns yellow, even in the dark, and brown when exposed to light; under water these changes take place less quickly (Fownes). According to Schwanert, the first portions of furfural which distil over (? in the rectification) soon become darker coloured when immersed in water, or kept in sealed tubes; but the latter portions remain nearly colourless, a fact which seems to indicate the presence of a more volatile impurity in the first portion. Pure furfural, which will not alter by keeping, can only be obtained by repeated rectification.

Furfural possesses great refracting power. It smells like a mixture of the oils of cinnamon and bitter almonds, and has an aromatic taste, like that of cinnamon-oil. Specific gravity 1.1648 at 15.6° C. (Fownes). Boils at 162.8—163.3° in metallic vessels with the barometer at 29.9" (Fownes), at 166° (Stenhouse), and volatilises unchanged. Vapour-density = 3.344 (Cahours), 3.49 (Fownes), calc. (2 vol.) = 3.328. It dissolves in 12 pts. water at 15.6° C. (Fownes), in 11 pts. at 13° (Stenhouse); it is very soluble in alcohol.

*Decompositions.*—1. Furfural is very inflammable, and burns with a yellow, very smoky flame.—2. When its aqueous solution is boiled with recently precipitated oxide of silver, metallic silver is deposited, and the filtered liquid yields by evaporation crystals of pyromucate of silver,  $C^6H^3AgO^3$ . Hence furfural is related to pyromucic acid in the same manner as common aldehyde to acetic acid. It likewise exhibits the characters of an aldehyde in combining with acid sulphite of sodium (*vid. inf.*).—3. Hot nitric acid converts furfural, with violent evolution of nitrous fumes, into oxalic acid.—4. Strong sulphuric acid dissolves it in the cold, without colour if pure, with purple-red colour if it contains metafurfural, and water added to the solution precipitates the furfural unaltered; but if the solution is heated, the furfural is decomposed and carbonised.—5. Strong hydrochloric acid acts on furfural in a similar manner.—6. With chlorine and bromine it forms resinous products. Iodine dissolves in it abundantly, without violent action.—7. Caustic potash dissolves furfural slowly in the cold, forming a dark brown liquid from which acids throw down a resinous substance; the same reaction takes place more quickly on heating the liquid.—8. Potassium with aid of heat, decomposes furfural with violence.

9. Furfural left in contact with ammonia for a few hours, is completely converted into furfuramide.—10. It dissolves in methylamine and ethylamine without decomposition in the cold, but if heated it blackens, and a blackish resinous substance separates containing only traces of nitrogen; these bases do not therefore act upon furfural in the same manner as ammonia (Wurtz).—11. With phenylamine, furfural forms a red colouring matter (Stenhouse, *Ann. Ch. Pharm.* lxxiv. 282). When an aqueous solution of furfural is added, with constant agitation, to a solution of phenylamine in acetic acid of ordinary strength, the mixture turns red, and if sufficient furfural solution has been added, becomes colourless after a while, and deposits a dark-coloured viscid substance, nearly insoluble in water, but soluble in alcohol, wood-spirit, and strong acetic acid; ammonia dissolves it, forming a colourless solution, but the red colour reappears on adding acetic acid. The red substance does not unite with mordants; it imparts a fine red colour to silk and wool, but the colour is very fugitive, fading quickly even in the dark. (Persoz, *Rép. Chim. app.* 1860, 220.)

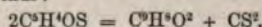
*Compound of Furfural with acid Sulphite of Sodium,  $C^6H^3NaSO^3$ .*—Pure furfural shaken up with a strong aqueous acid sulphite of sodium, dissolves and forms a solution, which, when evaporated over oil of vitriol, or better, when covered with an equal volume of strong alcohol and left to itself, deposits white or reddish laminae, having a fatty lustre; they may be purified by treatment with strong alcohol, and recrystallisation from water under a layer of alcohol. (Schwanert.)



*Sulphuretted and Seleniuretted Derivatives of Furfural.*

**Thiofurfol.**  $C^3H^4OS$ .—This compound, discovered by Cahours (Ann. Ch. Phys. [3] xxiv. 281), is produced by the action of sulphydric acid gas through a solution of furfural, or by slowly passing sulphydric acid gas through a solution of furfural in a large quantity of alcohol, and washing the precipitated powder with alcohol. As thus prepared, it is a yellowish crystalline powder; but if the sulphuretted hydrogen be passed quickly through a warm concentrated alcoholic solution of furfural, the thiofurfol separates in the form of a resin, but with the same composition.

Thiofurfol melts when heated, and yields a crystalline sublimate, having the composition  $C^3H^4O^2$ ; probably thus:



Thiofurfol, heated in contact with the air, diffuses a strong repulsive odour, and burns with a bluish flame, somewhat smoky, and with the odour of sulphurous acid.

The compound  $C^3H^4O^2$ , purified by two crystallisations from alcohol, appears in colourless or yellowish, iridescent, long, hard, easily friable needles. It is violently attacked by nitric acid, and converted into oxalic acid. It is insoluble in cold water but dissolves sparingly in hot water, whence it crystallises on cooling; tolerably well in ether; also in alcohol, especially when warm, forming a solution, which slowly turns brown on exposure to the air. (Cahours.)

**Seleniofurfol.**  $C^3H^4OSe$ .—Selenhydric acid acts upon furfural similarly to sulphydric acid, the clear liquid becoming turbid and depositing seleniofurfol in the form of a resinous, very unstable substance. (Cahours.)

**FUSCITE.** See SCAPOLITE.

**FUSEL-OIL.** In the alcoholic fermentation of potatoes, corn, and the mare of grapes, there are always formed, together with common alcohol, volatile oily bodies, which, for the most part, boil at higher temperatures than the ethylic alcohol, and therefore pass over with the latter portions of the distillate in the process of rectification. These oily products, designated by the general name of fusel-oil, resemble each other in their taste and smell, which are nauseous and fiery, and likewise agree in composition, in so far as they all contain ethylic and amylic alcohols; but most of them contain in addition, fatty acids and ethers, and some contain other members of the alcohol-series,  $C^3H^3+2O$ , the nature and quantity of these products varying considerably, according to the source from which the fusel-oil is derived, and the circumstances of the fermentation.

Potato-fusel-oil usually consists almost entirely of ethylic and amylic alcohols, the latter constituting the greater quantity; it may be freed from ethylic alcohol by agitating it with water, which dissolves the ethylic, with only a small proportion of the amylic alcohol, separating the oily liquid by a tap-funnel, and rectifying (see AMYLIC ALCOHOL, i. 203). Some samples of potato-fusel-oil, however, contain tetrylic or butylic alcohol,  $C^4H^{10}O$ , in addition to the preceding; in fact, it was in rectifying a sample of this kind of fusel-oil, that Wurtz made the discovery of tetrylic alcohol (Compt. rend. xxxv. 310). This alcohol has likewise been found in the fusel-oil from beet-molasses. (Wurtz, Ann. Ch. Pharm. xciii. 107.)

In fusel-oil from the brandy distilled from mare of grapes, Chancel (Compt. rend. xxxvii. 410) found tritylic alcohol,  $C^3H^4O$ ; and from the portion of the same kind of fusel-oil less volatile than amylic alcohol, Faget (*ibid.* 730) obtained a liquid which he supposed to be hexylic alcohol,  $C^6H^{14}O$ ; but this result is doubtful. (See HEXYLIC ALCOHOL.)

Most kinds of fusel-oil contain several members of the series of fatty acids,  $C^3H^3+2O^2$ .

Rowney (Chem. Soc. Qu. J. iv. 372) found in fusel-oil from the Scotch distilleries, water, ethylic alcohol, amylic alcohol, and a coloured oily residue insoluble in water, and containing capric acid in the form of caprate of amyl.

Wetherill (Chem. Gaz. 1853, p. 281) found in neutral-fusel-oil obtained as a residue in the preparation of alcohol, partly from wheat, partly from maize, acetic and caprylic acids, together with (less distinctly indicated) formic, caproic and  $\alpha$ -naphthyllic acids; also amylic and a little ethylic, but no butylic alcohol.

Fehling (J. Pharm. [3] xxv. 74) found in fusel-oil from the spirit of beet-molasses, several volatile fatty acids (capric, caprylic, &c.), and a neutral fat, answering nearly to the formula  $C^{22}H^{42}O^4$ , or  $C^{22}H^{42}O^4$ . When heated, it gave off the odour of acrolein, and when saponified, yielded capric acid.

Fusel-oil from beet-molasses has also been examined by A. Perrot (Compt. rend. xlv. 309) with the following results. The portion which distilled between  $80^\circ$  and  $110^\circ$  C. contained ethylic, tetrylic and amylic alcohols, without any appreciable portion of tritylic alcohol. The liquid remaining, after the amylic alcohol had been distilled, passed over between  $140^\circ$  and  $300^\circ$ . It consisted chiefly of compound



ethers, the only substance of more simple constitution contained in it being a *fœtid* liquid,  $C^8H^{16}O$ , which distilled at about  $200^{\circ} C.$ , floated on water, and did not exhibit the reaction of an alcohol with perchloride of phosphorus. The portion of the above-mentioned residue which passed over between  $140^{\circ}$  and  $200^{\circ}$  was heated for some time to  $100^{\circ}$  with caustic potash-solution, and the upper layer of the product distilled by itself. The greater portion, containing ethylic, tetrylic, and amylic alcohols, distilled between  $94^{\circ}$  and  $135^{\circ}$ ; the small portions which distilled between  $140^{\circ}$  and  $190^{\circ}$  did not contain hexylic or octylic alcohol, and the residue, which passed over between  $190^{\circ}$  and  $202^{\circ}$ , consisted of the above-mentioned compound,  $C^8H^{16}O$ . The mixture of acids, separated from combination with the potash, contained in small quantity (probably) valerianic, caproic, and cœnanthyllic acids, in larger quantity, caprylic and pelargonic acids. (See also A. Müller, J. pr. Chem. lvi. 103; Jahresber. 1851, p. 498.)

Capric acid has been found in potato-fusel-oil by S. W. Johnson. (J. pr. Chem. lxvii. 262.)

In rum fusel-oil from Surinam, G. J. Mulder (Jahresber. 1858, 302) found an unsaponifiable waxy body, together with palmitic acid, cœnanthic acid, and a very small quantity of cœnanthic ether. (See *Ure's Dictionary of Arts*, &c. ii. 313.)

*Defuselation of Alcohol.*—As fusel-oil imparts to alcohol a very unpleasant taste and smell, it becomes a matter of great importance to the distiller to remove it from all spirit intended for drinking. The complete removal of the fusel-oil is, however, a matter of considerable difficulty, and indeed is seldom attained on the large scale. Simple distillation will not effect the object, although the boiling points of ethylic and amylic alcohols differ from one another very considerably, common alcohol boiling at  $79^{\circ} C.$  and amylic alcohol at  $132^{\circ}$ . If, however, the spirit be diluted with water before rectification, and the strong spirit which comes over at first be collected apart, and this operation repeated several times, a tolerably pure spirit will at length be obtained, though at considerable expense and loss. In the modern stills constructed so that the more condensable portions of the vapour may be liquefied and flow back again, by far the greater portion of the fusel-oil is thus removed at once, together with the water, and a comparatively pure distillate is obtained. Still, however, a certain portion of the fusel-oil always diffuses into the alcohol-vapour and passes over with it.

For the complete defuselation of spirit, various methods have been devised, but that which is most generally adopted consists in absorbing the fusel-oil by *wood-charcoal*. To give the charcoal its full absorbing power, it must be recently ignited and left to cool in well-closed vessels; it is then reduced to coarse powder in rotating barrels containing a few iron balls. To effect the defuselation with the smallest possible quantity of charcoal, the spirit may be made to trickle through a number of casks filled with the charcoal and placed one above the other. According to Lüdgersdorff (Dingl. pol. J. xc. 369), 2 quarts (or 2.28 litres) of spirit of 80 per cent. Tralles, require for defuselation the following quantities of different kinds of charcoal:—

	Potato-spirit. Ounces.	Corn-spirit. Ounces.
Lime charcoal . . . . .	1 $\frac{1}{4}$	2 $\frac{1}{4}$
Fir " . . . . .	1 $\frac{1}{4}$	2 $\frac{1}{4}$
Birch " . . . . .	2 $\frac{1}{4}$	3 $\frac{1}{4}$
Willow " . . . . .	3 $\frac{1}{4}$	6
Oak " . . . . .	4 $\frac{1}{4}$	8
Bone-black . . . . .	10	14

These numbers must however be understood as merely approximate expressions of the relative defuselising power of the several kinds of charcoal, inasmuch as the detection of small quantities of fusel-oil in spirit is a matter of considerable difficulty.

In practice, however, the treatment of spirit with charcoal in the cold is seldom adopted, since a large quantity of spirit remains in the charcoal and a considerable portion of it is lost by volatilisation during the transference of the saturated charcoal to the still; moreover this operation takes a great deal of time. For this reason it is more usual to add the charcoal to the spirit in the rectifying apparatus—which, however, is a bad method, and never yields spirit free from fusel-oil, at least in the first portions of the distillate; a better method is to pass the vapour of the spirit through an apparatus filled with charcoal, before it is condensed.

Various methods of defuselation have been proposed, but for the most part with indifferent results, which consist in adding to the charcoal certain chemical reagents that will act upon the fusel-oil; or in treating the alcohol with these reagents after defuselation with charcoal, and before rectification; or in using these reagents without the charcoal.

Peters (Dingl. pol. J. cviii. 79) introduces between the charcoal in the casks used in the cold-digesting process, a layer of fine pulverised *peroxide of manga-*

*nse* placed between two pieces of flannel. Hourier (*ibid.* cxvi. 68) uses charcoal mixed with half its weight of *slaked lime*, also for cold digestion; Z al hau (*ibid.* c. 80) uses charcoal with *soap-boilers' lye*. A method very generally practised, is the addition of solution of *chloride of lime* before rectification to the spirit previously defuselised with charcoal (1 lb. of saturated solution of chloride of lime to 150 litres of spirit). One-third of this quantity of chloride of lime is however sufficient, if, after it has been mixed with the spirit, an equivalent quantity of *chloride of zinc* be added, hypochlorite of zinc being then formed, which is easily decomposed (Dingl. pol. J. clviii. 378). Stein (*ibid.* cxxxviii. 429) causes the vapour of the spirit to pass through a mixture of 2 pts. *chloride of calcium* and 1 pt. *charcoal*, whereby it is defuselised and dehydrated at the same time. Knop (Pharm. Centr. 1847, p. 687) mixes the spirit with a solution of *cupric sulphate* precipitated by *potash*, then adds excess of the alkali, and digests for some time, whereby cuprous oxide is formed.

The use of lime alone, or of potash, or of strong sulphuric or nitric acid is not to be recommended, inasmuch as the two former exert but little action, and the acids produce compound ethers, which give the spirit a peculiar odour not exactly that which is desired, and at the same time do not completely decompose the fusel-oil. Hünefeld (Erdmann's Journ. f. technische Chemie, xi. 527) uses manganate of potassium (*mineral chamæleon*), which, however, acts upon the alcohol as well as upon the fusel-oil; also chloride of lime, which gives the spirit a somewhat unpleasant odour.

*Milk* has long been used as a defuselising agent (Erdm. Journ. f. techn. Chem. xv. 369), its action being probably due to the fat which it contains. Breton (Moniteur industr. 1858, p. 2308) states that *olive oil* shaken up with spirit containing fusel oil takes up the whole of that impurity, and when the whole is left at rest, settles down and may be separated by filtration. For operating on the large scale, he recommends that the spirit be filtered through a layer of pulverised pumice-stone slightly drenched with the oil. As soon as the oil in the pumice becomes saturated with fusel-oil, the filtration is interrupted, and steam at the pressure of 2 or 3 atmospheres is passed through the pumice; the fusel-oil then volatilises, and the oiled pumice may be again used for defuselising. According to Kletzensky (Dingl. pol. J. cxlviii. 150), good *soda-soap* dissolved in spirit (that prepared with the oleic acid of the stearic acid manufacture answers best) is capable of retaining 20 per cent. of its weight of fusel-oil when the spirit is distilled off from it, so that a distillate is obtained quite free from fusel-oil: 4 lbs. of soap are stated to be sufficient for defuselising 1 Prussian eimer (about 69 litres or 15 gallons) of spirit, whatever may be the proportion of alcohol contained in it. The soap after being used may be completely freed from fusel-oil by distillation with steam at a temperature above 100° C., and may then be used for defuselising fresh quantities of impure spirit. Lastly, Vandevelde (Dingl. pol. J. clvii. 240) states, that brandy may be completely freed from fusel-oil by cooling it to -15° C. the fusel-oil falling to the bottom. The brandy may then be decanted or filtered and rectified. The statement, however, requires confirmation.

The best mode of detecting the presence of fusel-oil in spirit is to allow the spirit to evaporate slowly, as by rubbing it on the hand, or rinsing a glass out with it and leaving it to stand till the odour of the ethylic alcohol is no longer perceptible; the smell of the fusel-oil, being then no longer disguised by the alcohol, becomes apparent. Diluting the alcohol with warm water likewise brings out the smell of the fusel-oil. The turbidity produced in silver solution by fuselated spirit does not afford a very trustworthy indication, since a like effect may arise from the presence of many other substances. Stein (Dingl. pol. J. clv. 159) places the spirit in a large glass together with dry porous chloride of calcium, by which the ethylic alcohol is gradually absorbed, and keeps the vessel covered for some time; the odour of the fusel-oil becomes very perceptible after about two hours. (Handw. d. Chem. 2<sup>te</sup> Aufl. ii. [3] 794.)

**FUSIBLE METAL.** An alloy of lead, tin and bismuth, which melts below the temperature of boiling water (i. 591).

**FUSION.** See HEAT.

**FUSTIC.** Two yellow dyes are known by this name, viz. *old fustic*, obtained from *Morus tinctoria*, and *young fustic* from *Rhus Cotinus*. (See DYEING, ii. 366.)

**FUSTIN.** The name given by Preisser to the colouring matter of *Rhus Cotinus*.

**FUSYL.** The radicle C<sup>6</sup>H<sup>9</sup>, homologous with xylyl, CH, vinyl, C<sup>2</sup>H<sup>3</sup>, &c.; sometimes called valyl.

*Disulphide of Fusyl*, C<sup>6</sup>H<sup>8</sup>S or C<sup>6</sup>H<sup>7</sup>S<sup>2</sup>, is obtained, together with other products, by distilling disulphochloride of amylene with excess of potash. It is a clear, colourless liquid, having a not unpleasant odour, of specific gravity 0.880 at 13° C., boiling at 112° C.; insoluble in water, miscible in all proportions with alcohol and ether. (Guthrie, Chem. Soc. Qu. J. xii. 125.)



## G.

**GABBRO.** The name given by the Italian artists, and by L. von Buch, to a rock essentially composed of felspar and diallage, called by the French geologists euphotide. Besides the essential constituents just mentioned, it contains talc, amphibole or actinote, garnets, grains of pyrites, &c. This rock is abundant in the Alps. It is found in great quantity among the rounded pebbles in the neighbourhood of the Lake of Geneva. Von Buch met with it on the elevated portions of Monte Rosa, forming considerable masses superposed on the micaceous schist, and mixed in several places with serpentine. The tops of the mountains of the territory of Genoa, which overlook the gulf of Spezzia, are composed principally of it. In Corsica it forms districts of somewhat considerable extent, whence is derived the *verde di Corsica*, a fine variety of this rock. The *nero di prato*, the *verde di prato*, the *granite di gabbro* of the Florentines, are merely diallages, habitually metalloid, and mixed sometimes with serpentine, sometimes with felspar or jade, which are brought from the mountains of Tuscany. (D'Aubisson.) U.

Gabbro is closely related to serpentine (v. Buch, *Geognostische Beobachtungen*, i. 45). G. Rose (Bull. Soc. géolog. [2] iv. 1061) observed at Zobtenberg, in Silesia, a stratified gabbro interposed between serpentine and granite, and resting on the latter. In some places it was converted into a green slate, at others into serpentine.

The gabbro, or euphotide, of Mont Genève has been examined by Delesse (Ann. Min. [4] xvi. 238). The felspar of this rock, which contains water, belongs to the triclinic system (p. 619), but does not constantly exhibit the same composition, approaching sometimes to labrador, sometimes to vospite, sometimes to anorthite, which is also the case in some of the porphyries of the Vosges. This gabbro also contains magnetic iron ore, frequently titaniferous or chromiferous iron pyrites, talc, and serpentine, the latter often in such quantity as to make it doubtful whether the rock should be called gabbro or serpentine. It likewise contains carbonates, generally a ferrous carbonate with lime and magnesia, which occurs in the felspar and diallage crystals, as well as in the general mass of the rock. The felspar is the predominating constituent; indeed, the properties of the entire formation do not differ much from those of felspar.

The composition of the entire rock is, according to Delesse, 45.00 silica, 26.83 alumina and ferric oxide, 8.49 lime, 13.90 magnesia, soda, and potash, and 5.78 carbonic anhydride.

The gabbro of Odern in the Vosges contains the same principal and subordinate constituents. At the points where it touches the transition-slate, the laminae of mica penetrate into this rock, and the gabbro passes by insensible gradations, sometimes into a kind of talcose slate, sometimes into a serpentine slate. The gabbro of Odern contains, in addition to the above constituents, amorphous quartz, calcspar, also epidote, asbestos, and small crystals of albite and axinite. (Delesse, Ann. Min. [4] xvi. 325.)

The following are analyses: *a.* Of a fine-grained gabbro at the entrance of the Radauthal, in the Harz, containing about equal quantities of labrador and diallage, with small quantities of magnetic iron-ore and traces of iron pyrites uniformly distributed through it (Keibel, Jahresber. d. Chem. 1858, p. 768); *b.* Of a rock resembling gabbro, occurring on the Bahammer mountain, near Christiania, containing augite, or hornblende, and diallage, more rarely, black mica (Kjerulf, *ibid.* 1855, p. 1001):

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	Fe <sub>2</sub> O <sub>3</sub>	Mn <sub>2</sub> O	Mg <sub>2</sub> O	CaO	K <sub>2</sub> O	Na <sub>2</sub> O	CaCl, CaF, and P <sub>2</sub> O <sub>5</sub>	Water and Loss by ignition.
49.14	15.19	6.85	8.52	0.05	6.64	10.50	0.28	2.26	1.01*	0.52 = 100.56
47.93	8.94	15.90	. . .	. . .	11.20	11.32	0.85	1.05	. . .	1.39 = 98.50

On the gabbro of Neurode in Silesia, see G. v. Rath (Pogg. Ann. xcv. 533; Jahresber. 1855, p. 999). On the relations between the occurrence of gabbro, greenstone, hornblende-rock, and other allied rocks, on the one hand, and of metalliferous veins on the other, see Burat (Ann. Min. [4] xiii. 351; Jahresber. 1847-8, p. 1284.)

**GABBRONITE.** Syn. with SCAPOLITE.

**GADINIC ACID.** A crystalline fatty acid, obtained from cod-liver oil. A turbid residue of this oil, after being heated and then cooled to 5° C., deposited crystalline laminae of this acid, which were purified by saponifying with soda, precipitating with basic acetate of lead, washing the dried precipitate with ether, decomposing the residue with hydrochloric acid, and recrystallising from alcohol. The acid thus purified, melted between 63° and 64° C., and solidified again in a distinctly crystalline form at 60°. From the analysis of the barium- and silver-salts, the formula of the acid

\* CaCl = 0.11; CaF = 0.09; P<sub>2</sub>O<sub>5</sub> = 0.81.



was concluded to be  $C^{23}H^{23}O^2.H$ ; which is very improbable. (Luck, Chem. Contr. 1857, 191.)

**GADOLINITE.**  $Y^4SiO^4$  or  $3YO.SiO^2$ . *Ytterbyte*. (Dana, ii. 211; Gm. iii. 409.)—A black mineral, inclining to brown or green. It is generally amorphous, but is occasionally met with in monoclinic prisms of about  $115^\circ$ . Cleavage imperfect. Transparent at the angles. Powder, greyish-green. Harder than felspar; readily scratches glass. Hardness = 6.6—7.0. Specific gravity = 4.0—4.35. Gadolinite is found in very small quantities only, disseminated amongst the pegmatites in the neighbourhood of Fahlun, and at Ytterby in Sweden. It is sometimes coated with carbonate of yttrium. It is a silicate of yttrium, and serves for the preparation of yttria; it likewise contains ferrous and cerous oxides, together with oxide of terbium and oxide of erbium. (?) (Mosander.)

*a. Splintery Gadolinite.*—Of splintery fracture. When this variety is heated before the blowpipe, it becomes suddenly incandescent, increases in density, and becomes insoluble in acids, generally evolving a little water, and swelling up to a white, cauliflower-like mass. Dissolves readily in borax, yielding a green bead (from ferric oxide). Karverfort gadolinite parts with but little water when heated, does not swell up, but fuses to a turbid, greyish, or reddish bead. Splintery gadolinite dissolves in hydrochloric acid, with separation of gelatinous silica; but after heating, it is insoluble.

*b. Vitreous Gadolinite.*—Of conchoidal fracture; becomes brilliantly incandescent when gradually heated, turning greyish-green, and swelling up slightly, increasing somewhat in density. Its edges blacken before the blowpipe, but it does not fuse. Behaves with borax and hydrochloric acid like *a*.

	<i>a.</i> Scherer.	<i>b.</i> from Ytterby. Berlin.
Potash . . . . .	. . . . .	0.19
Soda . . . . .	. . . . .	0.18
Lime . . . . .	0.23 . . . . .	1.30
Magnesia . . . . .	. . . . .	0.54
Cerous oxide . . . . .	. . . . .	7.90
Oxide of Lanthanum . . . . .	6.33 . . . . .	
Yttria . . . . .	44.96 . . . . .	50.00
Glucina . . . . .	10.18 . . . . .	
Ferrous oxide . . . . .	12.13 . . . . .	14.44
Silica . . . . .	25.59 . . . . .	25.62
Alumina . . . . .	. . . . .	0.48
	99.42	100.65

C. E. L.

**GADUIN.** A peculiar brown substance contained in cod liver oil. (De Jongh.)

**GAGATES.** The ancient name of *jet* (Dioscorides and Pliny), derived from the river Gagus in Syria, near the mouth of which it was found.

**GAHNITE** or *Automolite*.  $Al^2ZnO^2$  or  $ZnO.Al^2O^2$ . (Dana, ii. 104; Gm. v. 46.) A greenish or greyish mineral, sometimes transparent, but generally opaque. It crystallises in large regular octahedrons, often forming beautiful twin crystals. Its cleavage is octahedral and perfect. Hardness = 8.0. Specific gravity = 4.1—4.3. Powder, pale bluish-green. Harder than quartz. Gahnite has only been found at Fahlun, in Sweden, and at Franklin, New Jersey, disseminated amongst talcose slate.

Gahnite does not melt before the blowpipe. Heated with carbonate of soda, it does not dissolve, but concretes to a dark slag, which, when heated on charcoal, yields an incrustation of oxide of zinc. Dissolves with great difficulty and very sparingly in borax and microcosmic salt; dissolves in a mixture of borax and carbonate of soda, yielding a clear bead, coloured with ferric oxide. Insoluble in aqueous acids and alkalis.

	Abich.	
	Fahlun.	N. America.
Magnesia . . . . .	5.25 . . . . .	2.22
Oxide of Zinc . . . . .	30.02 . . . . .	34.80
Ferrous oxide . . . . .	5.85 . . . . .	4.59
Alumina . . . . .	55.14 . . . . .	57.05
Silica . . . . .	3.84 . . . . .	1.22
	100.10	99.88

C. E. L.

**GALACTIN.** A gelatin-yielding substance, said by Morin (J. Pharm. [3] xxv. 423) to exist in milk.

**GALACTITE.** A calcareous variety of natrolite, found at Kilpatrick and Bishoptown in Scotland. (Jahresber. d. Chem. vii. 840, ix. 861.)

**GALAM** or **SHEA BUTTER.** A solid fat, much resembling palm-oil, the produce of a species of *bassia* (*Bassia Perkinii*), indigenous in the interior of Africa; also of another tree, resembling the American oak, growing in West Africa. It softens at about 35° C. (95° F.), and melts completely at 43·3° C. (110° F.). It dissolves for the most part in boiling alcohol, and perfectly in cold ether, separating in crystalline needles by cooling or evaporation. By saponification, it yields margaric acid. (R. D. Thomson and E. T. Wood, Phil. Mag. [3] xxxiv. 350.)

**GALANGA** or **GALANGAL.** A name applied to several roots possessing aromatic properties. Two principal kinds are described, viz. *Galanga minor* and *Galanga major*. The former, which is most prized for its aromatic properties, is obtained from a plant of unknown species growing in China. It has a reddish colour, an aromatic odour, and very acrid taste. The greater galangal is the produce of a scitamineous plant, the *Alpinia Galanga*, of Willdenow, and a native of China and the Malayan archipelago. The roots are cylindrical; reddish-brown externally, and marked with whitish circular rings, lighter coloured externally; they have an agreeable aromatic odour, but less powerful than those of the lesser galangal, and a hot peppery taste. According to Bucholz, they contain in 100 parts:—0·50 volatile oil, 4·50 resin, 9·70 extractive matter, 8·20 gum, 41·50 mucilage, 21·65 woody-fibre, and 12·30 water. The root of *Kempeferia Galanga*, a scitamineous plant, growing in the mountainous districts beyond Chittagong, and formerly supposed to be the true galanga, yields a crystallisable principle called *kempferide* (*q.v.*) (Pelouze et Frémy, *Traité*, vi. 368; *Penny Cyclopædia*, xi. 35.)

**GALAEPECTITE.** See HALLOYSITE.

**GALBANUM.** A gum-resin, commonly supposed to be the produce of *Balan Galbanum*, an umbelliferous plant native of the Cape of Good Hope. This, however, is doubtful. It is imported from Ethiopia and other parts of Africa, and from Persia. It comes over in masses composed of white, yellowish, brownish-yellow, and brown tears, unctuous to the touch, softening betwixt the fingers; of a bitterish, somewhat acrid, disagreeable taste, and a very strong smell; generally full of bits of stalks, leaves, seeds, and other foreign matters.

Galbanum contains more resinous than gummy matter: one pound yields with alcohol upwards of nine ounces and a half of resinous extract; but the gummy extract obtained by water from the same quantity amounts only to about three ounces. The resin is hard, brittle, insipid, and inodorous. The gummy extract has somewhat of a nauseous taste. The whole smell, flavour, and specific taste of this juice reside in an essential oil, which rises in distillation both with water and spirit, and gives a strong impregnation to both. From a pound of galbanum are obtained, by distillation with water, six drachms of actual oil, besides what is retained by the water. In this respect galbanum agrees with asafetida, and differs from ammoniacum.

According to the analyses of Meissner and Pelletier, galbanum contains:—

	Meissner.	Pelletier
Resin . . . . .	65·8	66·86
Gum . . . . .	27·6	19·28
Vegetable mucilage . . . . .	1·8	
Volatile oil . . . . .	3·4	6·34
Water . . . . .	2·0	
Insoluble matter . . . . .	2·8	7·52
	103·4	100·00

The resin may be extracted by alcohol; it is of a dark yellow colour, transparent, and melts easily at the temperature of the water-bath. It contains, as the mean result of Johnston's analysis, 73·88 p.c. carbon, 8·45 hydrogen, and 17·67 oxygen. When heated to 120° to 130° C., it yields, amongst other products, an oil of a fine indigo-colour, and very soluble in alcohol, to which it imparts its colour. (Gerh. iv. 373.)

From the recent experiments of Mössner (Ann. Ch. Pharm. cxix. 257), it appears that galbanum, distilled with water, yields about seven per cent. of a volatile oil, isomeric with oil of turpentine,  $C_{10}H_{16}$ , which, after rectification, is colourless, has a density of 0·8842 at 9° C., and boils at 160°. It turns the plane of polarisation to the left, its specific rotatory power being 0·1857. Index of refraction = 1·4542. Like other camphenes, it forms a crystallisable compound with hydrochloric acid.

The residue of the distillation consists of a resinous mass, and a turbid liquid containing gummy and extractive matters. (This liquid, distilled with sulphuric acid, yielded an acid, the silver-salt of which was intermediate in composition between acetate and propionate of silver.) On boiling the resinous mass with

milk of lime, and precipitating the filtrate with hydrochloric acid, a honey-yellow resin was obtained, soluble in alcohol and ether, containing from 71.93 to 72.05 p.c. carbon, and 8.0 to 8.2 hydrogen, agreeing nearly with Johnston's analysis above quoted. When heated to 100° with alcoholic hydrochloric acid, it yielded umbelliferone,  $C^8H^6O^2$ , a crystalline body previously obtained by Sommer (Arch. Pharm. [2] xcviii. 1), by the dry distillation of galbanum and other resins derived from umbelliferous plants. (See UMBELLIFERONE.)

The purified galbanum resin yields by dry distillation a small quantity of water and a greenish blue viscid aromatic oil, which, after a while, solidifies to a crystalline pulp: the oil may be separated from the crystalline matter by repeated boiling with water, and filtration through wet filters. The aqueous solution yields crystals of umbelliferone. The viscid oil, after being freed from the last traces of that substance by treatment with dilute potash, yields by repeated rectification a splendid blue oil,  $C^{20}H^{20}O$ , which boils at 289° C., is soluble in alcohol, insoluble in alkalis, is resinised by bromine, coloured green by alcoholic ferric chloride, and yellowish-red by nitric acid: in a freezing mixture, it quickly becomes viscid. By distillation with sodium, it yields (a) a colourless oil  $C^{20}H^{20}$ , boiling at 254°; and (b) by distillation with phosphoric anhydride, a yellowish oil,  $C^{10}H^{10}O$ , which boils between 250° and 253°. Hence the blue oil appears to be an alcohol,  $\left. \begin{matrix} C^{20}H^{20} \\ H \end{matrix} \right\} O$ , the oil *b* an ether,  $\left. \begin{matrix} C^{20}H^{20} \\ C^{10}H^{20} \end{matrix} \right\} O$ , and the oil *a* a hydride,  $C^{20}H^{20}.H$ . (Mössmer.)

**GALENA.** Native sulphide of lead. See LEAD, SULPHIDE OF.

**GALIPOT.** See TURPENTINE.

**GALITANNIC ACID.** See the next article.

**GALIUM.** The herb of *Galium verum* and *G. Aparine* contains citric acid, precipitable by neutral acetate of lead; galitannic acid, a peculiar variety of tannic acid, precipitable from the filtrate by basic acetate of lead, and consisting, in the hypothetically anhydrous state, of  $C^4H^2O^{10}$  (?) and rubichloric acid (*q.v.*), precipitated from the last filtrate (together with sexbasic acetate of lead) by ammonia. Galitannic acid is most abundant in *Galium verum*; citric acid in *G. Aparine*; and rubichloric acid occurs to about equal amount in both. (Schwarz, Ann. Ch. Pharm. lxxxiii. 57.)

In *Galium Mollugo*, L. (the entire plant, excepting the root), Vielguth (Chem. Centr. 1856, 423), found a camphor-like volatile oil, chlorophyll, fixed oil, wax, resin, albumin, starch, sugar, bitter principle, oxalic acid, a tannic acid which imparted a green colour to iron-salts (aspartannic acid), citric acid, and rubichloric acid. The air-dried plant yielded 7.6 per cent. ash, containing 14.5 per cent.  $K^2O$ ; 5.5  $Na^2O$ ; 23.4  $Ca^2O$ ; 7.6  $Mg^2O$ ; 0.3  $Al^2O^3$ ; 0.5  $Fe^2O^3$ ; trace of  $Mn^2O^3$ ; 1.3  $Cl$ ; 5.9  $SO^2$ ; 10.4  $P^2O^5$ ; 11.1  $SiO^2$ ; 4.0 sand; and 15.4  $CO^2$ .

**GALL.** See BILE.

**GALLAMIC ACID.**  $C^7H^7NO^4$ .—This acid, which has the composition of acid gallate of ammonium minus 1 at. water [ $C^7H^3(NH^4)O^3 - H^2O$ ], is obtained by adding to an alcoholic solution of tannin a mixture of 1 pt. of a concentrated solution of sulphite of ammonium and 5 pts. of strong ammonia, until the whole smells strongly of ammonia. The object of adding the sulphite is to prevent the oxidising action of the air. The liquor becomes heated, and gradually deepens in colour. It is evaporated to dryness, and repeatedly exhausted with boiling alcohol. On evaporating the alcoholic liquors, gallamic acid is deposited, and is recrystallised from water slightly acidulated with hydrochloric acid.

Gallamic acid crystallises in beautiful rectangular plates, having a fatty aspect, containing  $2C^7H^7NO^4 + 3aq$ . At 100° C. it loses its water (13.8 per cent.). It is very rapidly decomposed in presence of alkalis. E. A.

**GALLERYTHRONIC ACID.** See GALLIC ACID (p. 761).

**GALLHUMIC ACID.** Syn. with METAGALLIC ACID.

**GALLIC ACID.**  $C^7H^3O^5 = \left( \begin{matrix} C^7H^3O^5 \\ H^3 \end{matrix} \right)^m \left\{ O^2 \right.$  (Gm. xii. 396; Gerh. iii. 857.)

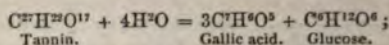
This acid, which was discovered by Scheele, exists, ready formed, in many plants, and is also obtained by the metamorphosis of gallotannic acid (tannin). It is contained in gallnuts, in sumach, in hellebore root, in dibidivi, in the acorns of *Quercus Eggylops*, in green and black tea, in *Uva ursi* leaves, in sandalwood, in colchicum, in strychnos bark, and in most astringent parts of plants.

To obtain it from plants which at the same time contain tannin, an infusion of the plant is precipitated with gelatin; the liquor separated from the filtrate is evaporated to dryness, and exhausted with alcohol; the alcoholic solution is evaporated; and the residue is exhausted by boiling water, which, on cooling, deposits gallic acid in crystals. They are purified by recrystallisation and treatment with animal charcoal.



Gallic acid is, however, much more conveniently obtained by the metamorphosis of the tannin in gallnuts (gallotannic acid). The gallnuts are powdered, and exposed to the air for about a month at a temperature of  $20^{\circ}$ – $25^{\circ}$  C., being kept continually moistened. The mass becomes covered with mould, which must be constantly removed. At the expiration of that time it is pressed. The liquor is coloured deep brown, but contains only a small quantity of gallic acid, the greater part of which remains in the residue. This is extracted by boiling water, and the crystals which deposit on cooling are redissolved in 8 times their weight of boiling water, and treated with animal charcoal. This method, though the least costly, requires a long time. The metamorphosis seems to depend on the action of a kind of nitrogenous ferment in the gallnut. If an extract of the gallnuts be employed, the metamorphosis also takes place, but much more slowly.

By the action of acids or alkalis, gallotannic acid is resolved into glucose and gallic acid:

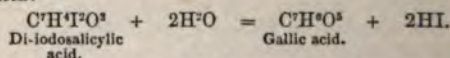


and this is the most convenient way of obtaining gallic acid.

According to Liebig, the best mode of proceeding is to precipitate a solution of tannin by sulphuric acid, and introduce the precipitate into boiling dilute sulphuric acid. After a few minutes, gallic acid is deposited in crystals. They are purified from sulphuric acid by repeated crystallisation, dissolved in boiling water, and acetate of lead added. The precipitate is washed, diffused in boiling water, and decomposed by sulphuretted hydrogen. The mixture filtered boiling, deposits coloured crystals on cooling.

Gallic acid may be also obtained from tannin by the action of alkalis; but this process is scarcely to be recommended, from the readiness with which gallic acid is oxidised in presence of potash.

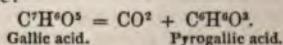
Lastly, gallic acid is produced by the action of hot concentrated potash-solution on *di-iodosalicylic acid*:



A considerable portion of the gallic acid thus formed is, however, converted during the process into pyrogallic acid. (Lautemann, Ann. Ch. Pharm. cxx. 317.)

Gallic acid crystallises in long silky needles, or in triclinic prisms. Observed combination,  $\text{oP} : \text{P} : \infty\text{P} : \infty\text{P}' : \infty\text{P}\infty$ . Inclination of the faces,  $\text{P} : \infty\text{P}\infty = 95^{\circ}$ ;  $\text{P} : \infty\text{P}' = 125^{\circ} 20'$ ;  $\infty\text{P}\infty : \infty\text{P}' = 84^{\circ}$ ;  $\infty\text{P}' : \infty\text{P} = 160^{\circ}$ ;  $\text{P} : \text{oP} = 116^{\circ}$ ;  $\infty\text{P}\infty : \text{oP} = \text{about } 150^{\circ}$ . Cleavage parallel to  $\text{P}$ ; less distinct parallel to  $\infty\text{P}\infty$ . The crystals are inodorous, and have an astringent slightly acid taste. They dissolve in 100 pts. of cold and in 3 pts. of boiling water, and the solution reddens litmus. They are very soluble in alcohol, less soluble in ether. They lose 2 at. = 9.5 per cent. of water at  $100^{\circ}$  C.

Pure and dry gallic acid heated to  $210^{\circ}$  or  $215^{\circ}$  C. decomposes into pyrogallic acid and carbonic anhydride:



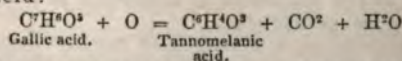
When gallic acid is kept for some time at  $230^{\circ}$  C., a brownish, lustrous, soluble residue is obtained, which precipitates gelatin, but not the vegetable alkalis. (Berzelius's gallulmic acid.)

When gallic acid is rapidly heated to  $250^{\circ}$  C., carbonic anhydride is given off; but instead of pyrogallic acid, a black ulmic compound is obtained, lustrous, tasteless, and completely insoluble in water. This is metagallic acid (*q.v.*) It is soluble in the alkalis, and its alkaline salts precipitate the salts of the earths and metals.

An aqueous solution of gallic acid does not change if excluded from the air; but in the presence of oxygen, more especially in the presence of alkalis also, carbonic anhydride is disengaged, and a black substance deposited.

Pure gallic acid precipitates neither gelatin nor the vegetable alkalis, a deportment by which it is distinguished from tannin; but, when mixed with gum, it produces a precipitate with gelatin.

Boiled with an excess of potash, gallic acid is changed into a black acid, tannomelanic acid:

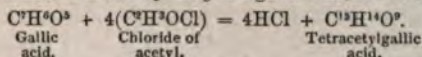


Solution of gallic acid, mixed with acid-carbonate of calcium and exposed to the air, becomes ultimately of a dark blue colour. When the solution is boiled, carbonate of calcium is deposited, and the liquid becomes colourless, but on cooling is again blue.

This coloration is said by Wackenroder to be due to the formation of a peculiar acid, called gallerythronic or cyanogallic acid.

Gently heated with concentrated *sulphuric acid*, gallic acid loses the elements of water, and becomes converted into *rufigallic acid*.

By the action of 4 at. of *chloride of acetyl* on gallic acid, *tetracetylgallic acid* is formed:



It crystallises in small lustrous needles, which are difficultly soluble in water; it is decomposed by the action of bases, forming gallates.

*Triacetylgallic acid*,  $\text{C}^7\text{H}^3(\text{C}^2\text{H}^3\text{O})^3\text{O}^3$ , *dibutyrylgallic acid*,  $\text{C}^7\text{H}^4(\text{C}^4\text{H}^7\text{O})^2\text{O}^3$ , and *dibenzoylgallic acid*,  $\text{C}^7\text{H}^4(\text{C}^7\text{H}^5\text{O})^2\text{O}^3$ , are similarly formed. (Nachbauer, J. pr. Chem. lxxii. 431.)

Gallic acid is decomposed by *permanganate of potassium*, with disengagement of carbonic acid; the decolorisation of the permanganate is so complete that a volumetric method for determining gallic acid has been based on this reaction. (Morin, Compt. rend. xvi. 577.)

Gallic acid reduces *gold* and *silver salts* to the metallic state.

Gallic acid expels carbonic acid from its salts; it is a tribasic acid, and forms three series of salts:

Trimetallic gallate	.	.	.	$\text{C}^7\text{H}^3\text{M}^3\text{O}^3$
Dimetallic gallate	.	.	.	$\text{C}^7\text{H}^4\text{M}^2\text{O}^3$
Monometallic gallate	.	.	.	$\text{C}^7\text{H}^5\text{M}\text{O}^3$

There are also basic and acid compounds. The alkaline gallates are soluble.

*Aluminium-salt.* This body has no definite composition. When freshly precipitated hydrate of alumina is added to a solution of gallic acid, the latter is entirely precipitated, while the former is not altered in appearance.

An *acid ammonium-salt*,  $\text{C}^7\text{H}^3(\text{NH}^4)\text{O}^3 + \text{H}^2\text{O}$ , is prepared by saturating a solution of gallic acid in absolute alcohol with ammoniacal gas. The salt which deposits is washed with alcohol, and then dissolved in the smallest quantity of boiling water. It crystallises in fine needles.

The *neutral* or *triammonic gallate* is not known.

*Antimony-salt.*—White precipitate obtained by the double decomposition of tartar-emetic and an alkaline gallate.

*Barium-salt*,  $\text{C}^7\text{H}^3\text{BaO}^3$ .—Freshly precipitated carbonate of barium is added to a boiling solution of gallic acid, as long as effervescence is produced: the liquor diluted, filtered, and evaporated, yields crystals, which must be removed as rapidly as they are produced. The more rapid the concentration, the purer the crystals.

The *calcium-salt*,  $\text{C}^7\text{H}^3\text{CaO}^3 + \text{aq.}$ , is prepared in like manner. Thin pale yellow crusts composed of adherent needles.

*Cobalt-salt*,  $\text{C}^7\text{H}^4\text{Co}^2\text{O}^3 + 3\text{H}^2\text{O}$ .—Deposited as a crimson powder when acetate of cobalt is boiled with excess of gallic acid solution, and the mixture evaporated.

*Lead-salt*,  $\text{C}^7\text{H}^4\text{PbO}^3 + \text{aq.}$ —Obtained as a white precipitate, which becomes crystalline, by adding acetate of lead to an excess of a boiling solution of gallic acid.

*Basic lead-salt*,  $2(\text{C}^7\text{H}^4\text{PbO}^3).\text{Pb}^2\text{O}$ .—When gallic acid is added to an excess of a boiling acetate of lead solution, a white flaky precipitate is formed, which, by boiling, is converted into a yellow crystalline basic salt of the above composition.

*Iron-salt.*—Ferric solutions colour gallic acid of a deep blue. When the liquid is heated, it becomes decolorised, and carbonic acid is liberated, the ferric salt being reduced to the state of protoxide. According to Mahla, part of the gallic acid is converted into metagallic acid (*q.v.*)

*Magnesium-salt*,  $\text{C}^7\text{H}^4\text{MgO}^3 + 2\text{H}^2\text{O}$ .—Obtained by boiling acetate of magnesium with excess of gallic acid, evaporating to dryness, and treating with alcohol to remove free gallic acid. The gallate of magnesium forms a light white powder, difficultly soluble in water.

*Manganese-salt*,  $\text{C}^7\text{H}^4\text{MnO}^3 + \text{aq.}$ —Obtained by double decomposition, as a white granular, crystalline powder, which rapidly becomes brown in the air.

*Nickel-salt.*—A basic nickel-salt of variable composition is prepared by treating gallic acid with carbonate of nickel.

*Potassium-salt*,  $2\text{C}^7\text{H}^3\text{KO}^3.\text{C}^7\text{H}^3\text{O}^3 + \text{H}^2\text{O}$ .—As this salt is rapidly changed by contact with the air, its preparation requires special precautions. An alcoholic solution of potash is gradually added to an alcoholic solution of gallic acid, until the precipitate, which at first disappears, begins to be permanent. If the liquid be then agitated, the precipitate separates in white flakes. These are filtered and washed with alcohol to remove free gallic acid, and then dissolved in water, concentrated, and precipitated by alcohol in colourless needles.



**Sodium-salt**,  $C^7H^3NaO^3 + 3H^2O$ .—Prepared in the same manner, and consists of fine needles, which lose their water of crystallisation at  $100^{\circ}$ .

**Strontium-salt**,  $C^7H^3SrO^3 + 2H^2O$ .—Prepared like the barium-salt, and consists of small needles, little soluble in water and insoluble in alcohol.

**Tin-salt**,  $C^7H^3Sn^2O^3 \cdot Sn^2O$ .—White crystalline powder, obtained by adding gallic acid to a solution of protochloride of tin, previously neutralised with ammonia.

**Zinc-salt**,  $C^7H^3Zn^2O^3 + Zn^2O$ .—Deposited as a bulky white precipitate when gallic acid is added to an excess of solution of acetate of zinc. E. A.

**GALLICINITE.** Syn. with RUTILE.

**GALLNUTS, GALLS, or NUTGALLS.** *Noix de galle. Galläpfel.*—Excrecences produced on the leaves and leaf-stalks of the dyer's oak (*Quercus infectoria*) by the punctures of the gall-wasp (*Cynips folii quercus* s. *Diplolepis gallæ tinctoriæ*), made for the purpose of depositing the eggs. The excrecence, in its early state, forms a spongy mass, enclosing the eggs; at a later stage it hardens, and is perforated by the insects as they make their escape.

The best galls, containing the largest quantity of tannin, come from the Levant, and among these the most highly prized are the black, blue, or Aleppo galls. They are heavy, compact, prickly, of blackish or brownish colour, and not eaten or perforated. The *white galls*, which are less valued, are generally somewhat larger, of yellowish-grey colour, much lighter, spongy, and perforated by the completely developed insect.

Inferior kinds of gallnuts, called *Trieste galls*, are obtained from Dalmatia, Illyria, and Calabria, where they grow chiefly on the *Quercus Cerris*: they are smaller, prickly on the surface, and of brownish colour.

Davy found, in the best Aleppo galls, 26.0 per cent. tannic acid, precipitable by immersed animal membrane; 2.5 mucus and extractive matter; 6.0 gallic acid; 2.5 calcium- and other salts; and 63 insoluble fibre. According to Guibourt, gallnuts contain 65.0 per cent. tannic acid, 2 gallic acid, 2 ellagic and luteogallic acids, 0.7 volatile oil and chlorophyll, 2.5 brown matter, 2.5 gum, 2 starch, 10.5 woody fibre, 1.3 sugar, albumin, and inorganic salts, and 11 water.

The galls, or oak-apples, of the common English oak are similarly constituted, but contain only a small proportion of tannic acid.

Galls are extensively used for the preparation of ink, for the production of black and grey tints in dyeing, for turkey-red dyeing, and in calico printing. The galls of the common oak and *Quercus Cerris* are used for tanning in Hungary, Dalmatia and the southern provinces of Austria. (See *Ure's Dictionary of Arts, &c.*, ii. 320.)

**GALLOTANNIC ACID.**  $C^7H^3O^{11} = (C^7H^3O^{11})^m \cdot O^3$ . *Tannic acid. Tannin. Tanning principle.* (Devreux, J. Phys. xlii. 401.—Séguin, Ann. Chim. xx. 15.—Braconnot, *ibid.* l. 376.—Pelletier, *ibid.* lxxxvii. 103.—Berzelius, *ibid.* xciv. 318.—Pelouze, Ann. Ch. Phys. liv. 337.—Liebig, Ann. Ch. Pharm. x. 172.—Büchner, *ibid.* liii. 175, 349.—Stenhouse, Phil. Mag. [3] xxii. 417; xxiii. 331; Proc. Roy. Soc. xi. 401.—Wetherill, J. Pharm. [3] xii. 107.—Mulder, Ann. Ch. Pharm. xxxi. 124.—Wackenroder, J. pr. Chem. xxv. 28.—Strecker, Ann. Ch. Pharm. lxxxi. 248; xc. 328; Chem. Soc. Qu. J. v. 102; Phil. Mag. [4], viii. 157.—Roehleider and Kavalier, J. pr. Chem. lxxiv. 28 and 399.—Gm. xv. 449.—Gerh. iii. 847.)

This acid is contained in the gallnuts of *Quercus infectoria* and other species of oak, in the various species of sumach (Stenhouse), and in Chinese gallnuts, the excrecences formed on the branches of a tree growing in Japan, which, according to Schenck (N. Repert. Pharm. v. 26 and 306), is also a species of sumach (*Rhus semialata*, or *Rh. Chinensis*).

Many other plants contain substances which resemble gallotannic acid in many respects, viz. in having a slight acid reaction, and an astringent but not acid taste; in precipitating albumin and gelatin from solution, and uniting with animal membrane into a substance which resists putrefaction, namely leather, the skin then becoming *tanned*. All these substances, called tannic acids, or tannins, were originally supposed to be identical with gallotannic acid, or to differ from it only in consequence of the admixture of foreign matters; but the more exact investigation to which they have been submitted of late years, has shown that most of them differ in some essential properties from gallotannic acid, this acid, indeed, existing only in the plants above mentioned.

The various species of tannin may be divided into two genera—those which give black or blue, and those which give olive-green precipitates, with ferric salts; and Stenhouse has shown that most of the tannins which give bluish-black precipitates with ferric salts are glucosides, that is to say, they are resolved, by boiling with dilute acids, into glucose and another substance—a property first pointed out in the case of gallotannic acid, which yields glucose and gallic acid, by Strecker; whereas, among those which give green precipitates with ferric salts, only one, viz. the tannin



of willow-bark, appears to be a glucoside. Among the tannins of the first division, gallotannic acid is especially distinguished by yielding pyrogalllic acid when heated, whereas the other tannins yield different products. (See TANNIN.)

*Preparation of Gallotannic acid.*—1. A percolating apparatus is half filled with finely pulverised gallnuts, and commercial ether, containing water and alcohol, is poured in. The liquid which runs away separates into two layers, the lower of which is a heavy, syrupy, amber-coloured solution of tannic acid, water, and ether; while the upper is mobile, consisting of ether, water, gallic acid, and a small quantity of tannic acid. Ether is poured into the apparatus as long as the lower stratum continues to increase: the upper layer is then removed; and the lower is repeatedly washed with ether, and dried in vacuo or by heat. Gallnuts thus treated yield from 35 to 40 per cent. tannic acid. (Pelouze, *Ann. Ch. Pharm.* x. 145, 210.)

2. 100 pts. of powdered gallnuts are treated in the percolating apparatus with a mixture of 300 pts. ether, 16 pts. alcohol of 90 per cent., and 5 pts. water (or 20 pts. alcohol of 69 per cent.); the residue, after the liquid has run off, is twice treated with the same mixture, then three times with pure ether; and the whole of the extracts are shaken up together, and left to settle for a week. The upper of the two layers thus formed is decanted from the syrup below, the latter is evaporated over the water-bath, and the residue is dried between 100° and 110° C. To purify the tannic acid thus obtained, or by the first process, from admixed gallic acid, ellagic acid, volatile oil, and chlorophyll, 100 pts. of it are shaken up with 100 pts. water and 200 pts. ether, whereby three layers are formed, the upper consisting of ether, the middle of aqueous gallic acid and impure tannic acid, while the lowest, which is syrupy, and amounts to 215 pts., leaves, on evaporation, 90 pts. of pure tannic acid (Guibourt, *Ann. Ch. Pharm.* xlviii. 359). Mohr employs for the extraction a mixture of equal volumes of ether and alcohol of 90 per cent. The filtrate is syrupy, but thinner than that obtained by the first method, and forms only one layer, exhibits but little turbidity on the addition of a large quantity of ether, and if 7 fluid ounces of ether are used to 2 ounces of galls, yields a quantity of tannic acid amounting to 72 per cent of the galls. If a mixture of 4 vols. ether and 1 vol. alcohol of 90 per cent. is used, the extract has the same constitution (Mohr, Sandrock). With Chinese galls, hydrated ether acts better than ether-alcohol. (E. Riegel, *N. Jahrb. Pharm.* iii. 252.)

According to Strecker, tannic acid, prepared and purified as above, cannot be further resolved into different substances by repeatedly treating its ethereal solution with water, but exhibits the same composition before and after this treatment. Rochleder and Kawaler, on the other hand, regard the tannic acid obtained from gallnuts by exhaustion with ether and water, as a mixture still containing gallic and ellagic acids; to separate these substances they proceed as follows:—

The solution of tannic acid in the smallest possible quantity of water, is shaken up with a small quantity of solution of neutral acetate of lead; the filtrate is mixed with water, and filtered again from the very impure tannate of lead thereby precipitated; and the new filtrate is precipitated by neutral acetate of lead in three portions. By decomposing the first and third of these precipitates with sulphydric acid, and expelling the excess of that acid by a stream of carbonic acid, solutions are obtained which, when boiled with sulphydric acid out of contact with the air, yield a large portion of ellagic acid. If the tannic acid solution, obtained in like manner from the middle portion, be precipitated by tartar-emetie, with addition of a little carbonate of ammonia, —the precipitate washed with hot water, and decomposed under water with sulphydric acid,—and the excess of that acid expelled by passing carbonic acid into the hot liquid, the filtrate, when left to itself in vacuo, becomes turbid, and deposits a brown substance. The solution, separated from this substance by filtration and evaporation in vacuo, leaves colourless amorphous tannic acid, which, when boiled with hydrochloric acid, no longer leaves any residue of ellagic acid.

*Properties.*—Gallotannic acid is a colourless, amorphous mass, remaining, when its aqueous solution is evaporated, in transparent, vitreous, shining, fissured, easily friable lumps. It is inodorous; has a strongly astringent taste, not at all bitter; reddens litmus strongly; does not soften between the fingers. It acquires a yellow colour by exposure to light, even in closed vessels. It does not act on polarised light.

Gallotannic acid dissolves readily in water, forming a colourless frothing liquid. The following table exhibits the specific gravity of aqueous gallotannic acid at 15° C. according to Hammer (*J. pr. Chem.* lxxxi. 169):

Per cent.	Sp. gr.	Per cent.	Sp. gr.
1 . . . . .	1.0040	6 . . . . .	1.0242
2 . . . . .	1.0080	7 . . . . .	1.0283
3 . . . . .	1.0120	8 . . . . .	1.0325
4 . . . . .	1.0160	9 . . . . .	1.0367
5 . . . . .	1.0210	10 . . . . .	1.0409

Gallotannic acid is precipitated from its aqueous solution by several salts, as by sal-ammoniac, common salt, sulphate and acetate of potassium (not by nitre or Glauber's salts, according to Strecker); by sulphuric and hydrochloric acid (Berzelius); from very concentrated solution by phosphoric, oxalic, and tartaric acid (Wackenroder), and by arsenic acid (Berzelius). When boric acid is dissolved, with aid of heat, in aqueous tannic acid, the mass solidifies on cooling to a white jelly, which dries up to a bulky, snow-white mass (Berzelius). These precipitates were regarded by Berzelius as compounds of tannic acid with mineral acids; but the precipitate thrown down by sulphuric acid retains, after pressure, only a small and variable quantity of sulphuric acid; that produced by hydrochloric acid gives off all its hydrochloric acid in vacuo over quicklime: hence the precipitates can be regarded only as mixtures of tannic acid with mineral acids, produced because tannic acid is less soluble in acids than in pure water. (Strecker.)

Gallotannic acid dissolves in *hydrated* more abundantly than in *absolute alcohol* (Pelouze). According to Pelouze, Bolley, and Laboldt, it dissolves but sparingly in *anhydrous ether*, and, when covered with it, remains perfectly pulverulent, according to Strecker and others, while, according to Mohr, it dissolves in considerable quantity. With *ether containing water*, it forms, after some seconds, a very heavy liquid, like that which separates in the preparation of tannic acid (p. 763). Of the two layers thus formed, the lower consists of tannic acid, which has taken up the water of the ether and only a very small quantity of ether, while the upper layer contains ether, a small quantity of tannic acid, and the foreign substances taken up with it (Pelouze). When tannic acid, dried at 110° C., is covered with anhydrous ether, the solution standing above the excess of pulverised tannic acid, after being agitated for a considerable time, contains in solution only 0.206 per cent. at 5° C., and 0.384 per cent. at ordinary temperatures. On adding to the ether half a volume per cent. of water, the tannic acid, which has hitherto been greyish yellow and pulverulent, deliquesces to brownish lumps, and on addition of a few drops more water, to a syrup. After addition of 1 vol. per cent. of water, the supernatant ether contains 1.2 per cent. tannic acid in solution. On continuously dropping water into the mixture and agitating, three layers are formed, the lowest of which is syrupy, and contains 0.297 grms. tannic acid in a cubic centimetre. The middle layer is somewhat lighter than the lowest, and contains in a cubic centimetre 0.082 grms. tannic acid dissolved in a large quantity of water and a small quantity of ether. The syrupy layer contains both ether and water, and is perhaps a tannate of ethyl and hydrogen, analogous to ethylsulphuric acid. (Bolley, Chem. Soc. Qu. J. xiii. 295; Ann. Ch. Pharm. cxv. 63.)

Gallotannic acid (crude) dried at 150° C. remains pulverulent when covered with 10 pts. of anhydrous ether, while the supernatant ether takes up 2 or 3 per cent. of solid constituents, chiefly the foreign substances mixed with the tannic acid. Water, either present in the ether, or subsequently added, is greedily absorbed by the tannic acid, and causes it to deliquesce to a viscid mass or a syrup, which does not mix with the excess of ether. When a solution of 100 pts. tannic acid in 100 pts. water is mixed with 150 pts. ether, the liquid, if agitated and left at rest at a temperature of 18° C. separates into three layers, the lowest of which has a specific gravity of 1.07, takes up half the total space, and contains 40.5 per cent. tannic acid, 42.2 ether, and 17.3 water. The middle layer, which has a density of 1.02, contains 14.15 per cent. tannic acid, 10.09 ether, and 75.76 water; the uppermost, of density 0.752, is chiefly ether, containing in solution small quantities of foreign matters and water. Also, when 20 grms. tannic acid, 39 grms. ether, and 20 grms. water are shaken up together and then left at rest, three layers are formed, the lowest of which increases by continual agitation at 14.5°, at the expense of the upper, till it occupies 36.5, and the upper 17.5 pts. of the entire space, the middle layer, which remains unaltered, occupying 20 pts. The bottom layer, when removed with the pipette, is found to be soluble in 4.5 to 5.5 pts. of water, more abundantly in lukewarm than in cold water. But if water be added to the mixture as it stands, divided into three layers, a quantity equal to 11 times the volume of the bottom layer will be required to dissolve it (the top layer at the same time diminishing to  $\frac{1}{2}$ ) because the water dissolves the bottom layer only so far as it can take up ether. Water saturated with ether dissolves only  $\frac{1}{2}$  of the bottom layer. The bottom layer is therefore hydrated *tannic acid*, containing ether in solution; the middle layer is *water* containing ether and tannic acid; and the top layer is *ether* which has taken up water, tannic acid, and the foreign constituents (Lubolt, J. pr. Chem. lxvii. 357). According to Mohr, on the contrary (Ann. Pharm. lxi. 352), the lowest of the three layers contains tannic acid dissolved in water; the middle layer tannic acid dissolved in ether. This statement, and another made by Mohr to the effect that tannic acid deliquesces to a syrup in anhydrous ether, and that by addition of more tannic acid, the ether may be completely converted into this syrup, are not reconcilable with the experiments above described.



The viscid syrup, which separates at the bottom of the mixture of gallotannic acid, water, and ether, unites with the supernatant ether, on addition of alcohol, to a thin filterable liquid. (Mohr.)

Gallotannic acid dissolves in *acetone*, with evolution of heat, the solution drying up to a jelly and leaving a powder which has the aspect of gallotannic acid. (Knop.)

Gallotannic acid does not unite with *urea* (Hlasiwetz, Wein. Akad. Ber. xx. 208). It does not dissolve in *picamar* (p. 162) even at the boiling heat (Reichenbach, Schw. J. lxxviii. 355). It dissolves in 6 pts. *glycerin* (Cap and Garot, J. Pharm. [3] xxvi. 81); in *bitter almond oil*, in almost all proportions, the solution, which turns brown in contact with the air, slowly depositing crystals of benzoic acid (Knop). It dissolves in other oils, both *fixed* and *volatile*.

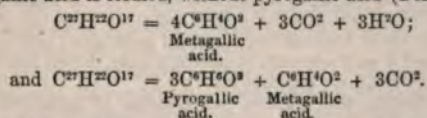
*Detection and Estimation of Gallotannic Acid.*—This acid is precipitated from its aqueous solution by *mineral acids*, as a gelatinous mass insoluble in excess of the acid. With *ferric salts* it forms a bluish-black precipitate; with *ferrous salts*, this precipitate forms only as the solution is gradually oxidised by exposure to the air. With *tartar-emetic* it forms a white gelatinous precipitate. With solution of *gelatin*, it forms a white precipitate, not absolutely insoluble in water, unless the tannic acid is in excess, in which case the precipitate is greyish, and aggregated to an elastic mass. It is owing to this property that tannic acid combines with animal skin, forming leather. It is entirely removed from a solution by immersing in it a piece of skin; and the acid may be estimated by determining the increase in weight of the skin. With most *organic alkaloïds*, gallotannic acid forms white compounds, insoluble in water, soluble in acetic acid.

*Estimation of Gallotannic Acid in Gall-nuts, &c.*—1. The aqueous extract is mixed with solution of gelatin, as long as a precipitate is thereby produced, the quantity of tannic acid which the same solution of gelatin (or another of known strength) is capable of precipitating having been determined by a previous experiment (Wheeler, Mem. Chem. Soc. iii. 319.—Fehling, Pharm. Centr. 1853, 872.—G. Müller, Chem. Centr. 1859, 42). Müller mixes the gelatin-solution with  $\frac{1}{2}$  pt. alum to accelerate the clarification of the liquid. To obviate the necessity of filtering, or waiting for the slow deposition of the precipitate towards the end of the experiment, Wheeler dips into the solution a glass tube loosely closed at the bottom with sponge, and tries whether the gelatin solution which enters the tube still gives a cloud with solution of gelatin.

—2. Stein mixes the aqueous extract with a known volume of a standard solution of neutral acetate of lead, dilutes the mixture to a given volume, and determines the quantity of lead remaining in a measured portion of the filtrate (Schweiz. polyt. Zeitschr. ii. 169).—3. Moneir (Compt. rend. xlv. 577; Dingl. cxlviii. 209) mixes the aqueous extract with solution of permanganate of potassium, which rapidly decomposes tannic acid, the quantity of tannic acid which this solution is capable of decomposing having been previously determined.—4. Hammer (J. pr. Chem. lxxxi. 159) determines the specific gravity of the solution (p. 763), both before and after the removal of the tannic acid by addition of about a fourfold quantity of animal skin which has been softened in water, pressed between linen, then washed, dried, and pulverised.

On the estimation of tannic acid see also Fr. Müller (N. Br. Arch. xxxviii. 147), Löwenthal, J. pr. Chem. lxxxi. 150; Handtke (*ibid.* lxxxii. 345); H. Sackur (Ueber den Gerbprocess, Dissertat. Berlin, 1860).

*Decompositions.*—1. Gallo-tannic acid heated to 150° or 160° C. becomes darker from incipient decomposition (Strecker); at 215° it is resolved into water, carbonic anhydride, and pyrogallic acid, which volatilise, and metagallic acid, which remains. At 250° only metagallic acid is formed, without pyrogallic acid (Pelouze):



The two decompositions may go on simultaneously. (Strecker.)

2. Gallotannic acid, heated in a platinum spoon, decrepitates, undergoes semifusion, swells up, carbonises, takes fire, and burns with a bright flame, leaving an easily combustible cinder (Berzelius).—3. Exposed on a watch-glass to strongly *ozonised air*, it acquires a yellow or yellow-brown colour, becomes glutinous and fluid, strongly acid, from formation of oxalic acid, and if the action be continued long enough, disappears completely, being converted into water and carbonic acid (Schönbein, J. pr. Chem. lxxxi. 12). Aqueous gallotannic acid, through which *ozonised air* is passed, absorbs it quickly and completely, becomes dark brown-red, then again lighter, and forms oxalic acid and a substance which reduces cupric oxide, these products being decomposed by the further action of the ozone, so that the liquid ultimately leaves



but little residue when evaporated (Gorup-Besanez, Ann. Ch. Pharm. cx. 106). When a very dilute aqueous solution of gallotannic acid is exposed to the air, it becomes turbid, from separation of grey crystalline gallic acid; oxygen is absorbed at the same time, and an equal volume of carbonic anhydride is produced (Pelouze). Aqueous gallotannic acid, evaporated with aid of heat in open vessels, leaves a brown, translucent mass, which, when treated with water, leaves a dark-brown residue; and by repeated evaporation and re-solution, a further quantity of the same substance is obtained (Berzelius). This residue is the *oxidised tannic acid* of the older chemists. Peroxide of hydrogen, and oxygenated oil of turpentine, do not produce any perceptible alteration in gallotannic acid. (Schönbein.)

4. Aqueous gallotannic acid dissolves finely divided *iodine*.—5. Aqueous *iodic acid* eliminates from gallotannic acid, even in the cold, carbonic anhydride mixed with a small quantity of carbonic oxide (Millon, Compt. rend. xix. 272).—6. *Bromine* acts violently on gallotannate of potassium, and forms a brown resin (Cahours, Ann. Ch. Phys. xix. 507).—7. By a small quantity of *chlorine*, aqueous gallotannic acid is clouded, coloured brown, and altered in the same manner as by evaporation in contact with the air; a larger quantity of chlorine decomposes it completely (Berzelius). Chlorate of potassium scarcely exerts any action upon it. (Simon.)

8. Strong *sulphuric acid* dissolves gallotannic acid with lemon-yellow or brown-yellow colour, becomes purple-red, and gives off sulphurous acid when moderately heated; and at a stronger heat becomes pitch-black, and forms humic acid (Wackenroder). By boiling, or by continued digestion at a moderate heat, with *dilute sulphuric acid*, gallotannic acid is resolved into gallic acid (Liebig), and dextroglucose (Strecker, see p. 762). Small quantities of ellagic acid and humous substances are likewise formed, probably as secondary products (Strecker). Acetic acid is not produced in this reaction. (Liebig.)

9. When gallotannic acid is boiled with aqueous *hydrochloric acid* out of contact with the air, ellagic acid and sugar are almost always obtained, their quantities, however, not bearing any definite proportion to one another. (Rochleder and Kawalier.)

10. *Nitric acid* does not precipitate aqueous gallotannic acid, or with difficulty only, but colours it yellow, then red, and decomposes it quickly with formation of oxalic acid (Stenhouse).—11. When aqueous gallotannic acid is mixed with aqueous *osmic acid* of the strength of 3 per cent., an inodorous deep blue liquid is formed, transparent only in thin films, and leaving on evaporation a black-blue, amorphous, insoluble layer. On dissolving this residue in aqueous osmic acid, osmic oxide is separated, the reaction being accelerated by heat; and the red-brown filtrate obtained after heating the liquid with ammonia yields, by evaporation, brown crystalline needles and a humous substance. The needles contain oxalic acid, and an acid very much like suberic acid. (Buttlerow, J. pr. Chem. lvi. 207.)

12. Gallotannic acid, boiled with excess of weak *potash-ley*, yields gallic acid (Liebig, xii. 398). The solution separated from the gallic acid does not contain acetic acid. By prolonged boiling, the gallic acid is resolved into carbonic and pyrogallic acids. (Liebig.)

When gallotannic acid is treated with *alkalis* in a current of hydrogen, gallic acid and a gum,  $C^{12}H^{22}O^{11}$ , are produced (Rochleder and Kawalier, Wien. Akad. Ber. xxv. 558).—13. Gallotannic acid boiled with *hydrate of barium*, yields gallic acid and glucate of barium (Rochleder and Kawalier). Baryta or limewater in excess quickly colours gallotannic acid green, blue, red, and yellowish-brown; acids decolorise the solution. (Wackenroder.)

14. When gallotannic acid is boiled for several hours with an equal weight of *neutral sulphite of sodium or potassium* and 12 pts. of water, or when the solution is evaporated till it froths up in viscid bladders, a quantity of gallotannic acid is obtained, equal to 75–79 per cent., and 5 or 6 per cent. of a second body, which has the composition, but not the properties, of sugar. (Knop.)

15. *Chromic acid*, heated with an aqueous solution of gallotannic acid, quickly decomposes it, with evolution of carbonic anhydride (Hünefeld, J. pr. Chem. xvi. 361). Acid chromate of potassium produces a yellow-brown precipitate, which quickly turns black (Wackenroder).—16. *Peroxide of manganese* heated with aqueous gallotannic acid, with or without sulphuric acid, decomposes it, with evolution of carbonic anhydride and formation of brown extractive matter. No gallic acid is produced in this reaction (Hünefeld). By *permanganate of potassium*, aqueous gallotannic acid is rapidly oxidised, the solution, if concentrated, giving off carbonic anhydride. In this reaction, a body of undetermined constitution is produced, besides carbonic acid and water (Monier, Compt. rend. xvi. 577). One milligramme of gallotannic acid, dissolved in a litre of water, is sufficient to decolorise the acid solution of the permanganate (Monier). When permanganate of potassium is added to a strongly acid solution of gallotannic acid, the colour of the permanganate disappears quickly at first (the

liquid becoming yellow and then colourless); more slowly, if a portion of the gallotannic acid has been decomposed, so that the instant at which the last portion of the gallotannic acid disappears cannot be recognised with certainty; 100 pts. gallotannic acid take up about 60 pts. oxygen from the permanganate. (Mohr, *Titirbuch*, 2 Aufl. Braunsch. 521.)

17. Gallotannic acid reduces *ferrie solutions*, partially at common temperatures, completely at the boiling heat, to ferrous solutions (Wackenroder; see p. 768).—  
18. From *cupric salts*, it reduces cuprous oxide; from *mercuric chloride*, mercurous chloride; from solutions of *mercurous* or *mercuric oxide*, it gradually throws down metallic mercury (Wackenroder). *Carbonate of silver* is reduced by gallotannic acid, even in the cold. (Schiff, *Ann. Ch. Pharm.* cix. 65.)

19. Aqueous gallotannic acid, which remains unaltered when not exposed to the air, decomposes, with evolution of carbonic anhydride and formation of gallic acid—if it remains in contact with the nitrogenous constituents of the gall-nuts; therefore, in infusion of galls, and more quickly in gall-nuts moistened with water (Robiquet, Pelouze). Ellagic acid is formed at the same time (Erdmann, Mulder). The formation of mould, which commonly takes place, has no influence on the transformation (Winckler, *Répert.* 53, 401). The decomposition takes place even in closed vessels (Nesenbeck, *Br. Arch.* xxxi. 129), and more quickly in proportion as the solution of tannic acid is more dilute (Robiquet). The transformation may be regarded as a fermentation process, inasmuch as it is stopped or retarded by antiseptic substances, as alcohol, wood-vinegar, creosote, mercuric oxide, and corrosive sublimate, and gall-nuts freed from tannic acid excite vinous fermentation in solution of sugar (Larocque). The pectase of the gall-nuts is the ferment which excites the gallous fermentation, and the simultaneous conversion of the pectose into pectin. The pectase of gall-nuts is also capable of converting the pectin of fruits into pectic acid; and pectase from turnips can excite the gallous fermentation. Gallotannic acid prepared with ether, but not purified, still contains sufficient pectase to give rise to its decomposition when dissolved in water. Emulsin, yeast, vegetable or animal albumin, and legumin retard rather than promote the gallous fermentation. (Robiquet.)

**Gallotannates or Tannates.** Gallotannic acid is tribasic, forming *neutral* or *trimetallic salts*, having the composition  $C^{27}H^{19}M^3O^{17}$ ; likewise *acid* and *basic salts*. All these salts, however, alter quickly in contact with the air, and are difficult to obtain pure; hence but few of them have been analysed. The acid expels carbonic acid from carbonates, and forms precipitates with the solutions of most metallic salts.

**Tannate of Aluminium.**—Hydrate of aluminium shaken up with aqueous gallotannic acid, quickly unites with it, forming a compound which is insoluble in water, but soluble in excess of tannic acid.

**Tannate of Ammonium**,  $C^{27}H^{21}(NH^4)O^{17}$  (?)—Carbonate of ammonia added to aqueous tannic acid, throws down a white precipitate, which changes to a white powder in vacuo (Berzelius). An excess of carbonate of ammonia causes the white precipitate produced at first to disappear immediately, and the liquid, after standing for some time, acquires a red-brown colour, and deposits light white flocks (Buchner). Ammonia gas passed to saturation into a solution of tannic acid in absolute alcohol, throws down white flocks, or, if the solution is very strong, a white resin, which becomes friable when repeatedly treated with absolute alcohol. This substance, dried between filtering paper, and then over oil of vitriol, forms a resin having a faint brown tint, and very soluble in water. (Buchner.)

The salt dried over sulphuric acid, gives by analysis 51.3 per cent. carbon, 4.5 hydrogen, and 3.3 nitrogen, agreeing approximately with the formula above given.

**Tannate of Antimony** is a white, gelatinous, sparingly soluble precipitate, obtained by mixing solution of tartar-emetic with gallotannic acid. Its composition resembles that of the ferric salt. (Pelouze.)

**Tannates of Barium.**—*a.* Baryta-water, added to aqueous gallotannic acid, throws down a basic salt (Berzelius). The precipitate dissolves in aqueous gallotannic acid, not in excess of baryta-water; it turns green when left to stand, or washed in contact with the air, also if it has been prepared with baryta-water not in excess.

*b.* When carbonate of barium is added to aqueous gallotannic acid as long as effervescence takes place, the liquid then filtered, and the filtrate concentrated, only small quantities of flocks separate on cooling, but alcohol added to the brown solution throws down a white light powder, which, after washing with alcohol, turns brown in drying.

*c.* From warm aqueous solutions of alkaline tannates, chloride of barium throws down a white precipitate, sparingly soluble in cold water, more soluble in boiling water (Berzelius). The light flocculent precipitate assumes a very faint reddish colour when washed, and after drying at 100° C. contains 39.7 per cent. C, 28 H, 36.8 O, and 20.7 BaO (Buchner). Strecker regards the salt as a mixture of tribarytic and dibarytic tannate.



*Tannate of Cadmium.*—Hot aqueous gallotannic acid throws down from cadmium-salts a white precipitate, which assumes a yellow-green colour when dry, becomes anhydrous at  $100^{\circ}$ , and contains 21.4 per cent.  $\text{Cd}^{\circ}\text{O}$ . Insoluble in water and in alcohol. (Schiff.)

*Tannate of Calcium* is obtained as a white precipitate, on mixing the concentrated solutions of tannate of ammonium and chloride of calcium; the precipitate is soluble in pure water. When a solution of gallotannic acid is mixed with excess of hydrate of lime, a nearly insoluble *basic salt* is produced, the solution retaining only traces of gallotannic acid.

*Tannate of Chromium.* (?)—Chromic hydrate forms with aqueous gallotannic acid, an insoluble compound, which is likewise precipitated on mixing a solution of a chromic salt with gallotannic acid (Berzelius). According to H. Rose, chromic salts are not precipitated by infusion of galls.

*Tannate of Cobalt.*—Cobalt-salts form a yellowish precipitate with infusion of galls.

*Tannate of Copper* is precipitated in bulky yellow flocks on adding gallotannic acid to a solution of cupric acetate. If, on the other hand, the copper-salt be added by drops to solution of tannin, a reddish white precipitate is formed, completely soluble in ammonia. According to Wackenroder, the ammoniacal solution is not precipitated by sulphydric acid.

*Tannates of Iron.*—*Ferrous Tannate* is a white gelatinous precipitate, formed on mixing the concentrated solutions of ferrous sulphate and gallotannic acid. Dilute solutions give no precipitate.

*Ferric Tannate.*—When a mixture of gallotannic acid and a ferrous salt is exposed to the air, the precipitate quickly acquires a bluish-black colour, being oxidised to ferric tannate. This black precipitate, which forms the colouring matter of common ink, is produced immediately on mixing a ferric salt with excess of gallotannic acid. The reaction is very delicate, indicating the presence of the smallest traces of tannic acid. If, on the other hand, the tannin solution is added drop by drop to an excess of the ferric salt, no precipitate is formed, the liquid not even becoming coloured; but the gallotannic acid is oxidised, and the ferric salt reduced to ferrous salt. The same reduction takes place when the black precipitate of ferric tannate is boiled with excess of tannic acid, carbonic acid being then evolved, and the mixture becoming colourless. The black precipitate dried in the air contains 12.02 per cent. ferric oxide, agreeing nearly with the formula  $\text{C}^{27}\text{H}^{10}(\text{Fe}^2)\text{O}^{17}$ , which requires 11.92 per cent. Wittstein, on the other hand, found the quantity of iron in the precipitate obtained by mixing tannic acid with ferric salts, very variable; the only way in which he obtained a constant compound was by precipitating ferrous sulphate with gallotannic acid, and exposing the precipitate to the air.

*Tannates of Lead.*—These salts vary in composition according to the proportions of the solutions used for precipitation; the variation extending from 3 to 10 atoms of lead for 27 atoms of carbon (Strecker). *a.* On mixing a solution of gallotannic acid with a quantity of lead-acetate not sufficient for complete precipitation, a white precipitate is obtained, which becomes slightly brown on exposure to the air. When boiled with water, it loses part of its acid, and leaves a compound containing 34.21 per cent. lead-oxide (Berzelius). This salt probably contains  $\text{C}^{27}\text{H}^{10}\text{Pb}^3\text{O}^{17}$  (calculation 36.2 per cent. lead-oxide.)

Gallotannic acid heated with lead-oxide, gives off 4.4 per cent. water, which is equivalent to the substitution of 3 at. lead for 3 at. hydrogen; the salt thus produced is, therefore, also the neutral salt,  $\text{C}^{27}\text{H}^{10}\text{Pb}^3\text{O}^{17}$ .

*b.* Another tannate of lead is obtained on pouring a solution of gallotannic acid into a boiling solution of acetate of lead. A yellow pulverulent precipitate is then formed, which may be obtained of constant composition, by boiling it for about a quarter of an hour in the liquid, in presence of excess of the lead-acetate and free acetic acid. It is nearly insoluble, and when dried at  $100^{\circ}$  C. contains 20.2 per cent. carbon, 1.1 hydrogen, and 63.0 to 63.8 per cent. protoxide of lead, answering to the formula  $\text{C}^{27}\text{H}^{10}\text{Pb}^3\text{O}^{17}.3\text{Pb}^2\text{O}$ , which requires 20.2 C, 1.1 H, and 63.0  $\text{Pb}^2\text{O}$  (Liebig, Ann. Ch. Pharm. xxvi. 128).—*c.* The precipitate formed by adding dilute aqueous tannic acid to excess of lead-acetate, if collected after a few minutes boiling, and dried in vacuo, contains 68.2 per cent. C, 1.0 H, 17.1 O, and 63.7  $\text{Pb}^2\text{O}$ , answering to the formula  $2\text{C}^{27}\text{H}^{10}\text{Pb}^3\text{O}^{17}.7\text{Pb}^2\text{O} + 3\text{H}^2\text{O}$  (calculation, 18.6 C, 1.3 H, 15.65 O, and 64.45  $\text{Pb}^2\text{O}$ ). When heated to  $120^{\circ}$  C., it gives off its water (15.64 per cent.), and then contains 64.7 per cent.  $\text{Pb}^2\text{O}$ , answering to the formula  $2\text{C}^{27}\text{H}^{10}\text{Pb}^3\text{O}^{17}.7\text{Pb}^2\text{O}$  (Strecker).—*d.* When a lukewarm aqueous solution of gallotannic acid is precipitated with excess of acetate of lead, and the precipitate washed with boiling water, it contains 24.85 per cent. C, 1.40 H, and 62.80  $\text{Pb}^2\text{O}$ , agreeing nearly with



the formula  $2C^{27}H^{10}Pb^{30}O^{17}.3Pb^{2}O + 3H^{2}O$  (calculation 25.11 C, 1.71 H, 21.09 O, and 52.09 Pb<sup>2</sup>O). At 120° C. it gives off its 3 atoms of water, amounting to 2.2 per cent. (Strecker.)

*Tannate of Magnesium* is obtained as a sparingly soluble basic salt, by digesting the aqueous acid with hydrate or carbonate of magnesium; if the magnesia is used in excess, the liquid retains only traces of tannic acid.

*Tannates of Mercury*.—The *mercuric salt* is a brick-red precipitate, insoluble in excess of mercuric nitrate, but soluble in hydrochloric acid, the solution gradually becoming turbid, from formation of mercurous chloride. The *mercurous salt* is obtained, on mixing the solutions of mercurous nitrate and gallotannate of potassium, as a yellow precipitate, which dissolves in excess of mercurous nitrate, the solution gradually depositing metallic mercury.

*Tannate of Nickel*.—Greenish white precipitate.

*Tannate of Platinum*. (?)—Tincture of galls added to solution of platinic chloride throws down pale yellow flocks.

*Tannates of Potassium*.—On adding alcoholic potash to a moderately concentrated alcoholic solution of gallotannic acid, till red veins become visible on the surface of the liquid, white crystalline flakes are produced, which when washed with alcohol, pressed and dried, are converted into an earthy salt, very soluble in water, and containing 45.0 per cent. C, 3.0 to 3.1 H, and 13.2 to 13.3 K<sup>2</sup>O, agreeing approximately with the formula  $C^{27}H^{10}K^{30}O^{17}$  (calculation, 46.9 C, 2.8 H, and 13.6 K<sup>2</sup>O).

Another potassium-salt, white, pulverulent, and less soluble, is obtained by dropping a moderately concentrated aqueous solution of gallotannic acid into a solution of carbonate of potassium.

*Tannate of Silver*.—Aqueous gallotannic acid forms a brown precipitate with oxide or with nitrate of silver.

*Tannate of Sodium*, which appears to contain  $C^{27}H^{10}Na^{30}O^{17}$  (at 100° C.), is obtained in the same manner as the corresponding potassium-salt. After drying over the water-bath, it forms a light, earthy mass, which, when suspended in water, becomes glutinous like gum-water, and dissolves easily in a larger quantity of water. It contains on the average 46.6 per cent. carbon, 3.3 hydrogen, and 10.6 anhydrous soda, the above formula requiring 48.9 C, 3.0 H, and 9.3 Na<sup>2</sup>O.

*Tannate of Tantalum*. (?)—Infusion of galls colours tannalic acid yellow, and precipitates tannalic anhydride of the same colour, from its acid and alkaline solutions. The light yellow precipitate is soluble in alkalis. (Rose.)

*Tannates of Tin*. (?)—Both *stannic* and *stannous hydrate* digested with infusion of galls decolorise it, and appear to abstract all the tannic acid. Infusion of galls precipitates stannic chloride, also stannous salts.

*Tannate of Titanium*. (?)—From hydrochlorate of titanic oxide neutralised as nearly as possible with ammonia, aqueous tannic acid throws down yellow-red flocks (Pfaff). From acid solutions of titanic acid, infusion of galls throws down a thick chocolate-coloured precipitate. Tannic acid colours *alkaline molybdates* deep blood-red, and on addition of hydrochloric acid, a blood-red precipitate is formed which dissolves in a large quantity of water. (Rose.)

*Tannate of Tungsten*. (?)—Infusion of galls produces no alteration in the solution of an alkaline tungstate, but acids, added to the mixture throw down a thick chocolate-coloured precipitate. (Rose.)

*Tannate of Uranium*.—Tincture of galls forms with uranic salts a red-brown precipitate. (Rose.)

*Tannate of Vanadium*. (?)—With *salts of vanadic oxide*, aqueous gallo-tannic acid forms a bluish inky mixture, which, when left to stand quietly, deposits a black precipitate. With *alkaline vanadates*, infusion of galls first gives a green, then an inky-black colouring; the mixture diluted with a large quantity of water forms a clear dark blue liquid, which gradually turns green in contact with the air. The concentrated mixture may be used as an ink, but changes in contact with the air, the black-blue colour passing into green. The writing is durable and withstands the action of hydrochloric acid, of chlorine, or of alkalis, but is destroyed by successive treatment with chlorine and alkalis (Berzelius), or by nitric acid (Kraut).

*Tannate of Zinc* is a white precipitate obtained by adding an alkaline tannate to sulphate of zinc.

**GALLS.** See GALLNUTS (p. 762).

**GALLSTONES.** The general composition of these concretions in man and in the ox, as determined by Dr. Thudichum, has been already stated in the article BILIARY CALCULI (i. 588). The same analyst has recently made a more minute examination of a specimen of ox-gallstones, in which he has found the following constituents:

Glycocholate of sodium.  
 Cholonate of sodium.  
 Salt of resinous acid related to the preceding.  
 Cholic acid, partly combined with lime.  
 Choloïdic acid.  
 Cholochrome, free and combined.  
 Traces of cholesterin and fatty acids.  
 A new organic compound soluble in ether.  
 A sulphide emitting sulphuretted hydrogen with acids.  
 Lime and magnesia as carbonate, phosphate, and in combination with cholechrome and cholic acid.

Chloride of sodium.  
 Chloride of ammonium.  
 A compound ammonia-base.  
 A matter having a very repulsive odour, and another having the flavour of musk.  
 Iron in the form of oxide and phosphate.  
 Alumina.  
 Manganese.  
 Copper, a trace.  
 Zinc, in considerable quantity.

The bulk of the calculi was made up of cholochrome; next in amount were the biliary acids and their salts: then came lime and zinc and the new organic compound; the other ingredients were present in small quantity only.

The presence of zinc is certainly remarkable; its presence was probably due to some accidental cause, as from the animal having licked wood coated with zinc-paint.

For the method of analysis, see the original memoir (Chem. Soc. J. xiv. 34).

**GALLULMIC ACID.** See **GALLIC ACID** (p. 760).

**GALVANISM.** See **ELECTRICITY** (p. 412).

**GALVANOMETER.** An instrument for measuring the force of a galvanic current. It is often applied, however, to instruments which merely indicate the presence of a current (p. 460).

**GALVANOPLASTY.** Syn. with **ELECTRO-METALLURGY** (see *Ure's Dictionary of Arts, &c.*, ii. 88).

**GALVANOSCOPE.** The proper name for instruments which indicate the existence of galvanic currents without measuring them exactly (p. 443).

**GAMBIR.** See **CATECHU** (i. 816).

**GAMBOGE** or **CAMBOGE.**—*Gomme-gutte, Gummigutt.*—This gum-resin appears to be produced from the *Stalagmites cambogioides*, a tree belonging to the tribe of the *Guttiferae*, and growing in the peninsula of Cambogia, in Siam. From the bruised leaves and yellow branches of this tree, there flows a yellow juice, which is received in cocoa-nut shells or earthen vessels, then allowed to thicken, and afterwards formed into rolls. This is the finest sort, called the *pipe gamboge of Siam*. A portion is also formed into round cakes, either entire, or having a hole in the middle. Gamboge is also produced in Ceylon; and an inferior sort is said to be obtained from the *Gambogia gutta*, a tree growing wild on the Malabar coast.

Gamboge occurs in pieces of various sizes, of a dirty yellowish colour externally, and covered with a yellow powder. When broken, it exhibits a vitreous or conchoidal fracture, with brown or saffron-yellow colour. Its powder is of a brilliant yellow, and forms an emulsion with water. It is nearly inodorous at ordinary temperatures, but gives out a very peculiar odour when heated. When simply taken into the mouth, it has scarcely any perceptible taste, but if chewed for some time, it causes a sharp somewhat acrid feeling, ending in a sweet sensation, accompanied by dryness in the mouth. It afterwards excites a flow of saliva, which is coloured yellow. It is a drastic purgative.

Gamboge dissolves in alcohol, in resins, and in ammonia. The ammoniacal solution forms a red precipitate with salts of *barium*, yellow with *zinc* salts, reddish-yellow with acetate of *lead*, and brownish yellow with nitrate of *silver*.

The following analyses of gamboge are by Dr. Christison:

	Pipe-gamboge from Siam.		Cake-gamboge from Siam.		Ceylon gamboge.			
Resin . . .	74.2	71.6	64.3	65.0	68.8	71.5	72.9	75.5
Gum . . .	21.8	24.0	20.7	19.7	20.7	18.8	19.4	18.4
Amylaceous matter . . .	. . .	. . .	. . .	6.2	5.0			
Woody fibre . . .	. . .	. . .	4.4	6.2	6.8	5.7	4.3	0.6
Moisture . . .	4.8	4.8	4.0	4.6	4.6	. . .	. . .	4.8
	100.8	100.4	99.6	100.5	100.0	96.0	96.6	99.3

Cake gamboge is not entirely a natural product, but a manufactured article.

The resin contained in gamboge is easily separated by means of ether; it is hyacinth-red, and yields a powder of a very fine yellow colour. It possesses marked acid properties, decomposing alkaline carbonates at the boiling heat, and forming with

the alkalis red salts, which may be separated from their solutions by common salt, like soaps.

According to Buchner's analysis, the resin contains 72.04 per cent. carbon, 7.23 hydrogen, and 20.73 oxygen (mean), and its silver-salt, 18.7 per cent. oxide of silver, whence Buchner deduces for the resin the formula  $C^{72}H^{23}O^{18}$ ; and for the silver-salt the formula  $C^{72}H^{23}O^{18}.AgO$ . Johnston assigns to the resin the formula  $C^{70}H^{22}O^{18}$ .

Chlorine turns the resin white, and decomposes it. Nitric acid decomposes it at the boiling heat, forming oxalic and picric acids.

Gamboge is sometimes used in medicine as a purgative, but its administration requires great caution. Its principal use is as a pigment in water-colour painting.

Yellow juices, which, when inspissated, form a substance resembling gamboge, are obtained from several trees of the guttiferous and hypericaceous tribes. Some of them give good colours, but less permanent than that of real gamboge. An artificial gamboge is sometimes manufactured with turmeric and other materials. This should be rejected. (Gerh. iv. 474.—*Penny Cyclopædia*, vi. 176.)

**GAMSIGRADITE.** (Breithaupt, Jahresber. 1861, p. 986.)—A black amphibole from the timazite (*q.v.*) of Gamsigrad in Servia, where it occurs in crystals exhibiting the usual combinations of hornblende. Hardness = 5–6 (on the ordinary scale, 7 on that of Breithaupt); specific gravity = 3.119. It is velvet-black, with a glassy lustre, opaque, and yields a greenish-grey streak. According to R. Müller, it melts very easily and quietly before the blow-pipe, to a greenish black, strongly magnetic glass. It is but slightly attacked by hydrochloric acid. It contains:

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Mn <sub>2</sub> O <sub>3</sub>	Mg <sub>2</sub> O	Ca <sub>2</sub> O	Na <sub>2</sub> O	K <sub>2</sub> O
46.58	13.63	12.29	6.00	8.44	8.83	3.17	1.00 = 99.94

**GANGUE.** The stones which fill the cavities forming the veins of metals, are called the gangue or matrix of the ore.

**GANOMATITE.** Syn. with CHENOCOPROLITE (i. 867).

**GARANCEUX.** A product obtained by treating the waste madder of the dye-houses, which still contains a certain quantity of alizarin and other colouring matters, with sulphuric acid, to remove lime, magnesia, &c. It is adapted for dyeing red and black, but does not afford a good purple. (See MADDER.)

**GARANCIN.** The product obtained by treating pulverised madder, previously exhausted with water, with concentrated sulphuric acid at 100° C., and again washing with water. The residue thus obtained, is found to yield better results in dyeing than madder itself, the colours produced by it being more brilliant, and requiring less after-treatment, while the white portions of the fabric remain unsullied. (See MADDER.)

**GARBENSTILBITE.** Syn. with STILBITE.

**GARCINIA MANGOSTANA** (Resin of). The crude resin contains 87.9 per cent. pure resin soluble in alcohol, 8.3 per cent. gum soluble in water, and 3.8 per cent. insoluble matter, consisting of woody fibre and earthy substances. The residue obtained by evaporating the alcoholic solution is a transparent amorphous mass, having a lemon-yellow colour when pulverised, easily soluble in alcohol and in ether, only partially soluble in alkalis. It melts at 110° C., and consists of  $C^{72}H^{22}O^{18}$ . The ammoniacal solution of the purified resin, forms with neutral acetate of lead, an egg-yellow, gummy precipitate, which when dried at 110°, is said to contain  $5PbO.C^{72}H^{22}O^{18}$ . The residue obtained by evaporating the ammoniacal solution is greenish, melts at 80° C., and consists of  $C^{72}H^{22}O^{18}$ . The portion insoluble in ammonia is pale yellow, melts at 115°, and consists of  $C^{72}H^{22}O^{18}$ . (N. Reitler, Chem. Centr. 1858, pp. 510 and 575; Jahresber. 1858, p. 449.)

The rind of the fruit of this tree is used in the East Indian Islands as a remedy against fever; it contains a substance called mangostin (*q.v.*)

**GARDENIA GRANDIFLORA.** A Chinese plant, the pods of which yield crocin (p. 108.)

**GARNET.** *Grenat. Granat.*—This name comprehends a variety of minerals, all crystallising in the monometric or regular system, and represented by the general formula  $3MO.M^2O^2.2SiO^2$  (Berzelius),  $3MO.M^2O^2.3SiO^2$  (Gmelin), or  $M^2m^2SiO^4$  (Odling); wherein M = Ca, Mg, Fe, or Mn, and m = fr, al, or mn. Thus a variety of substances are met with differing in composition, but identical as to their constitution, known generally as garnets, but having each a distinctive name. According to Trolle Wachtmeister, all garnets may be considered as mixtures of the following kinds of garnet in varying proportions. The names inclosed in brackets after each formula designate the varieties of garnet in which that particular compound predominates:

1.  $Ca^2al^2SiO^4$  (*Cinnamon-stone, Grossularia and white garnet*).
2.  $Mg^2al^2SiO^4$  (*Black garnet from Arendal*).



3.  $Mn^2Al^2SiO_4$  (Garnet from North America and from Broddbo).
4.  $Fe^2Al^2SiO_4$  (Oriental *Almandine* and other red precious garnets).
5.  $Ca^2Fe^2SiO_4$  (Common yellow, brown and black garnet; also *Idena*).
6.  $Mg^2Fe^2SiO_4$
7.  $Mn^2Fe^2SiO_4$  } (These compounds do not predominate in any known species of garnet.)
8.  $Fe^2Fe^2SiO_4$  }

*Pyrope*, which consists principally of the compounds 1, 2, and 5, is characterised by containing chromium, which probably replaces part of the aluminium.

Garnet crystallises in rhombic dodecahedrons  $\infty O$  (fig. 178) or trapezohedrons 202 (fig. 180), more frequently, however, in the combinations  $\infty O . \infty O \infty$  (fig. 201), and  $\infty O . 202$  (fig. 206). Cleavage imperfect parallel to  $\infty O$ . (Kopp.)

The formula  $Ca^2Al^2SiO_4$ , where Ca is partly replaced by Mg, Mn, and Fe, and *ally* *fe*, likewise belongs to vesuvian, which, however, crystallises in forms of the dimetric system; hence the chemical compound represented by this formula is dimorphic. When grossularia from Wilui is melted, it becomes undistinguishable, both physically and chemically, from fused vesuvian from the same locality.

Garnets are generally transparent or translucent, rarely quite opaque; their colour vary from red or red-brown to yellow, white, green, and black, according to the metallic oxides which they contain. They have a vitreous or resinous lustre. Specific gravity = 3.15 to 4.3. Hardness = 6.5 to 7.5, or rather greater than that of quartz.

Garnet melts readily before the blow-pipe to a transparent glass; behaves with fluxes like vesuvian. The fused glass has a lower specific gravity than garnet. Garnet from Greenland has a specific gravity of 3.9; after fusion, only 3.05. Garnet is generally not attacked by hydrochloric acid, unless it contains a large proportion of lime, and then only partially; but, after fusion, it may be entirely decomposed by hydrochloric acid, with separation of gelatinous silica; a red heat is sufficient for this purpose when the garnet is rich in lime. (Kobell.)

The following are analyses of garnets:—1. C. Gmelin (Berz. Jahresb. v. 224).—2. Klaproth (Beiträge, v. 138).—3. Tr. Wachtmeister (Kongl. Vetensk. Vet. 1823).—4. Croft (G. Rose, Reise nach dem Ural, p. 132).—5. Wachtmeister (loc. cit.).—6. Hisinger (Schw. J. xxi. 258).—7. Kobell (ibid. lxxiv. 283).—8. Seybert (Sill. Am. J. vi. 155).—9. Hisinger (Berz. Jahresb. ii. 101).—10. Kersten (Karst. Arch. f. Min. iv. 388).—11. Wachtmeister, (loc. cit.).—12. Vauquelin (J. Phys. l. 94).—13. Damour (Institut. 1856, p. 1198).—14. Wachtmeister (Pogg. Ann. ii. 1).

#### Lime-garnet.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O	Mn <sub>2</sub> O	Mg <sub>2</sub> O	Ca <sub>2</sub> O	
1. Ceylon, Cinnamon stone .	38.80	21.20	6.50	. . . . .	. . . . .	. . . . .	31.25	= 97.75
2. Wilui, Grossularia .	44.00	8.50	12.00	. . . . .	traces	. . . . .	33.50	= 98.10
3. " " " .	40.55	20.10	5.00	. . . . .	0.48	. . . . .	34.86	= 100.99
4. Urals, white .	36.86	24.19	. . . . .	. . . . .	. . . . .	. . . . .	37.15	= 98.20

#### Magnesia-garnet.

5. Arendal .	42.45	22.47	. . . . .	9.29	6.27	13.43	6.53	= 100.44
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#### Iron-garnet or Almandine.

6. Fahlun .	39.66	19.66	. . . . .	39.68	1.80	. . . . .	. . . . .	= 100.60
7. Hungary, precious .	40.56	20.61	5.00	32.70	1.47	. . . . .	. . . . .	= 100.34

#### Manganese-garnet.

8. Haddam, Connecticut .	35.83	18.06	14.93	. . . . .	30.96	. . . . .	. . . . .	= 98.79
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#### Iron-lime garnet.

##### Melanite, Pyrenee.

9. Westmanland .	37.55	. . . . .	31.35	. . . . .	4.70	. . . . .	26.74	= 100.34
10. Schwarzenberg, green .	36.85	4.05	25.35	. . . . .	0.95	. . . . .	32.32	= 99.52
11. Vesuvius, brown .	39.93	13.45	10.95	3.35	1.40	. . . . .	31.66	= 100.74
12. Frascati, black .	34.00	6.40	25.50	. . . . .	. . . . .	. . . . .	33.00	= 98.90

#### Chrome-garnet.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O	Mn <sub>2</sub> O	Mg <sub>2</sub> O	Ca <sub>2</sub> O	
13. Bissorsk, Ural, Uvarowite .	35.57	6.26	23.45	. . . . .	. . . . .	. . . . .	33.22	= 98.50
14. Pyrope, Bohemia .	43.70	22.40	6.52	11.48	3.68	5.60	6.72	= 100.10

Garnets are almost always found crystallised, and disseminated amongst various rocks, especially mica-schist, gneiss, pegmatite, clay-schist, serpentine rocks, and cal-

careous rocks in the neighbourhood of crystalline deposits. They are also found in trachytic, basaltic, and volcanic earths of recent formation; and are then generally of that class known as *Melanite*, which contains ferric oxide. Garnet has also been found in small granular masses, and sometimes in small strata in mica-schist. (Beudant.)

*Altered Forms.*—Garnets containing ferrous oxide, often become rusty and disintegrated from oxidation of the iron, and are sometimes altered to red iron ore. The lime in lime-garnets may be taken up by the carbonic acid in waters, and if magnesia is combined with the carbonic acid (as acid carbonate), it may take the place of the lime, and thus give rise to a stratitic pseudomorph, or to a chlorite, if the iron partly remains. Quartz also occurs with the form of garnet. (Dana, ii. 194.) C. E. L.

**GAS.** The term gas, now commonly applied to aeriform substances, was introduced about the middle of the seventeenth century by Van Helmont; but its general use, even in scientific language, is of much more recent date. Strictly speaking, a gas is a substance possessing the condition of perfect fluid elasticity, and presenting, under a constant pressure, a uniform rate of expansion for equal increments of temperature, whereas vapour, which may be regarded as corresponding to gas near a state of maximum density, does not, under constant pressure, present a rate of expansion that is uniform for equal increments of temperature.

Since the liquefaction of several gases that were considered to be permanent, has been effected, the distinction between gas and vapour, originally established by Van Helmont, and since generally adopted, viz. that vapours could be reduced to a liquid or solid condition by increase of pressure and reduction of temperature, while gas could not be so altered, is no longer tenable, or, at most, it applies only to the ordinarily prevailing conditions of atmospheric pressure and temperature. Under great pressure, gases appear to approximate to the condition of vapour, and vapours, at high temperatures, assume the characters of gas.

Prior to the middle of the seventeenth century, the substantial nature of aeriform substances was almost unknown. It was considered that air, like fire, was an element of extreme subtilty, with a natural tendency to rise from the earth. Still it was held that air contributed to the formation of some substances, and even that it was a constituent part of them, but there was no decided opinion as to the material nature and ponderability of air.

A still greater vagueness prevailed with regard to the appreciation of the chemical characteristics and functions of air. It was known to be in some way necessary for the support of fire and of animal life; but its influence in regard to these phenomena seems to have been regarded more as analogous to the influence of light in vegetation than of that nature which it is now known to be.

As regards the existence of aeriform substances distinct from atmospheric air, it is very doubtful whether anything was known either by the ancients or by the alchemists. The suffocating or inflammable nature of the air evolved from the earth in various localities was early observed, and, under the terms *spiritus* or *flatus*, aeriform substances produced artificially appear to be referred to by some of the writers from the fourteenth to the seventeenth century. It seems, however, to have been generally considered that aeriform substances, differing in their characters from atmospheric air, were not essentially distinct, but that they differed from it only in consequence of admixtures. Thus, Basil Valentin, describing the inflammable air and suffocating air of mines, says, 'It must be remembered that choke-damp is so called because it is not pure air like that above ground, but always carries with it something that is thicker and more detrimental to man than the air above ground.'

The aeriform substances generated during chemical operations were, as a rule, but little regarded at this period. Paracelsus (1493–1541) mentions the evolution of gas in the solution of iron by sulphuric acid, as an eruption of air, but without attaching any significance to it. The knowledge of Libavius (15–?–1616) respecting aeriform substances, appears to have been limited to the inflammable and suffocating gases of mines.

Van Helmont (1577–1644) was the first to undertake the study of aeriform substances whose characters were different from those of atmospheric air, and to show that they could be produced artificially. He distinguished between gases and vapours, as being respectively permanent and condensable—"Gas est spiritus non coagulabilis." He showed that the conditions under which gases are generated are chiefly combustion, fermentation, putrefaction, and the reaction of acids with metals, calcareous substances, &c. But, at the same time, he was far from having any true conception of the relations between air, gas, and vapours, nor did he arrive at any knowledge of the distinctions between different kinds of gases.

Under the name of *gas sylvestre*, and more rarely *gas carbonum*, he described carbonic acid as being a product of the combustion of fuel, of fermentation, &c., and as existing

in mineral waters, in caverns, and in the stomachs of animals. He showed that it could be obtained from limestone by means of acids, that it would not support life, and that it extinguished flame. But he confounded under this term several other gases quite distinct from carbonic acid, such as nitric oxide, sulphurous acid, &c. The only distinction he appears to have drawn between gases was between what he termed *gas sylvestre* and the inflammable gases produced by the destructive distillation of organic substances and in putrefactive decomposition. Van Helmont also observed that when a light was burnt under a bell-jar over water, the air which remains after a time extinguishes the flame; but he gives no further account of this air, nor did he make any advance towards a knowledge of the part played by the atmosphere in combustion and animal respiration.

In the early part of the seventeenth century, even previously to the demonstration of the ponderability of air by Torricelli, in 1643, the influence and functions of atmospheric air began to attract the attention of chemists. One of the earliest and most remarkable inquiries into this subject was instituted by Jean Rey, a French physician, in consequence of a communication from an apothecary named Brun, that he had observed, in the calcination of tin and lead, an augmentation of weight in the calx obtained, which he was unable to account for. In 1630, Rey published a treatise on this subject, entitled "*Essays sur la recherche de la cause, pour laquelle l'étain et le plomb augmentent de poids, quand on les calcine,*" which, though chiefly of a speculative character, distinctly puts forward the opinion that the augmentation of weight observed in the calcination of metals was due to the absorption of air. At the same time, however, Rey, adopting the prevailing opinion of his period, that metals were compound substances, considered that the absorbed air combined with the calx pre-existing in the metal, and made it heavier than the metal from which it was obtained, in the same way that sand is made heavier by water adhering to it. He also pointed out that the augmentation of weight in the calcination of metals was limited and definite. "*L'air epaissi s'attache à la chaux, et va adhérer peu à peu aux plus minces de ses parties; ainsi son poids augmente du commencement jusqu'à la fin. Mais quand tout est affablé, elle n'en scaurait prendre davantage.*" This essay of Rey's was the first attempt to elucidate a phenomenon which, nearly a century and a half later, served as the key to a knowledge of gaseous substances, and furnished the basis of the present system of chemical science. It attracted, however, but little attention, and did not lead to any experimental investigation of the subject. Meanwhile the facts of the augmentation of weight in the calcination of metals, of the necessity of air for respiration and combustion, of its alteration by those processes, and, at a later period, the fact of the absorption of air in the calcination of metals, though perfectly well known and established, floated through the chemistry of the intervening period, unexplained and unappreciated, much as the facts of isomerism, allotropy, and catalysis remain, amidst the chemistry of the present day, without explanation or apparent connection with other facts.

But though the tendency of chemical investigation prior to the latter part of the eighteenth century, did not lead to the experimental study of these important phenomena in any degree commensurate with their actual value, their consideration in a more speculative manner was not neglected, nor was it without useful results. The direct study of aeriform substances was also prosecuted with some success. The inflammability of the air produced by the reaction of iron with dilute sulphuric acid, was made known by Turquet de Mayerne, in 1650, which may be regarded as the date of the recognition of hydrogen as a distinct substance.

In 1665 Hooke propounded in his "*Micrographia*" a theory of combustion, which was designed to afford an explanation of the necessity for the presence of air for its support. He considered that atmospheric air contained a substance analogous to it, not identical with that fixed in nitre, and possessing the property of dissolving all combustible substances, provided their temperature was raised sufficiently high. This solution he supposed to take place with such violence, that fire was produced, which in his opinion was simply a phenomenon of motion. The product of this solution might be aeriform, liquid, or solid. Combustion in a limited quantity of air was considered by him to cease, in consequence of the solvent becoming saturated with the combustible substance, and could be revived only by a fresh supply of air. The constituent of air which he regarded as thus taking part in combustion, existed in a highly fixed condition in nitre, so that a given bulk of nitre contained incomparably more of it than an equal bulk of air. Hooke's views were, however, put forward in such general terms as to be destitute of any scientific value, and are of interest rather as showing the absence, at that period, of true principles of chemical investigation, which might have led to discoveries of the highest importance, had they been applied under the influence of opinions which, in their general tendency, were so much allied to the more advanced knowledge of the present.



Hooke's views were subsequently developed by Mayow in his "*Tractatus de sal-nitro et spiritu nitro-aëreo*," published in 1669. His *spiritus nitro-aëreus*, existing both in air and in nitre, was the solvent which Hooke had assumed to be active in combustion. A similar theory was also propounded in reference to respiration and animal heat by Willis, in his "*Exercitatio de Sanguinis incaloescentia sive accensione*," published in 1671, with the difference that he regarded combustion as consisting, not only in the reaction of the combustible with a constituent of atmospheric air, but also in the simultaneous elimination of a combustible principle from the former.

Far more in accordance with the spirit of experimental investigation were the labours of Boyle, with regard to aeriform substances, and the related phenomena of combustion, respiration, &c. In his "*Continuation of new experiments physico-mechanical, touching the spring and weight of air and their effects, wherein are contained divers experiments, made both in compressed and also in factitious air*," &c., published in 1680, he showed that air could be produced artificially, and he was the first to collect the air thus produced, without mixture with atmospheric air. His examination of factitious air was, however, more physical than chemical. In his "*Tract containing suspicions about some hidden qualities of the air*" (1674), and in his "*General history of the air*" (1692), he frequently refers to the alteration of air in combustion, but his conclusions are more guarded than those of his predecessors. He was satisfied that, by respiration and by combustion, something was abstracted from the air, but he defines this only as "some vital substance diffused through the air, whether it be a volatile nitre, or (rather) some yet anonymous substance, sidereal or subterranean;" and referring to the views of Hooke and Mayow, he says, "though I agree with them in thinking that the air is in many places impregnated with corpuscles of a nitrous nature, yet, I confess, that I have not been hitherto convinced of all that is wont to be delivered about the plenty and quality of the nitre in the air; for I have not found that those that build so much upon this volatile nitre have made out, by any competent experiment, that there is such a volatile nitre abounding in the air."

In reference to combustion, and the calcination of metals, Boyle opposed the prevailing opinion that calcination was due to the separation of moisture or some other constituent of the metal calcined. The increased weight of the calx he ascribed to the combination of ponderable heat-substance, and this preconceived opinion led him to disregard many of his most important observations. In the course of his experiments, he clearly showed that in calcination, air is absorbed; but he made no attempt to connect this fact with the augmentation of weight. He heated tin and lead in sealed retorts containing air, and found that, after maintaining the heat for a considerable time, on opening the retort, air rushed in to supply the place of what had been absorbed by the metal. But he regarded this merely as a proof that the retorts had been hermetically closed. Nor did Boyle arrive at any knowledge of the mode in which air took part in, and was essential to combustion, though he showed, in his "*New experiments touching the relation betwixt flame and air*" (1672), that in a vacuum combustion could not take place, and that lead was converted into a calx only when in contact with air.

Simultaneously with Boyle, a similar explanation of the increase of weight in the calcination of metals was given by N. Lemery. In his "*Cours de chymie*" (1675), he says, "although by the action of fire, some sulphurous or volatile portions of lead are separated which ought to diminish the weight, nevertheless, after a long calcination, it is found that, in place of weighing less, as it should do, it weighs more;" and he ascribes this fact to the penetration of the fire-corpuscles into the pores of the lead.

In this respect, the views of Becher, Boyle, and N. Lemery, as to the increase of weight in calcination of metals, were identical; they were also accepted by the majority of chemists at the time, and were retained up to the commencement of the eighteenth century.

One of the earliest objectors to the opinion that glass vessels were permeable by the fire-corpuscles, as assumed by Boyle, was Cherubin D'Orleans, Capucin of the province of Touraine, who in 1679 published a dissertation "*Sur l'impenetrabilité du verre, . . . sur la cause de l'augmentation du poids de l'Etain et du Plomb par la calcination*." Referring to Boyle's experiment with lead in a sealed retort, he says, "these chemical observations do not at all convince me; they rather prove the impermeability of the glass than its permeability. . . . For to show the alleged permeability of glass by that experiment, he should, before opening the retort, have weighed it together with its contents; then having exactly ascertained the weight, he should have weighed it again with its contents, after having opened it, in order to ascertain whether the external air, which he says rushed in with noise when the retort was opened, did not cause an alteration of the weight that had been observed before opening the retort; . . . without doubt, we have found that the retort weighed more

after it was opened than it did before." This criticism of Boyle's experiment and conclusion noway affects the main object he had in view, viz. to establish the absorption of air in the calcination of metals; but it is highly interesting as illustrative of the growing sense of the importance of quantitative observations in chemical investigation, and more especially since the deficiency pointed out in Boyle's experiment was precisely that which, when subsequently supplied by Lavoisier, contributed so largely to the establishment of correct views of the calcination of metals.

About the commencement of the 18th century, the belief in the ponderable nature of heat became considerably shaken, and with its abandonment, the previous explanation of the increased weight of metallic calces fell to the ground. Those chemists who noticed it at all, put forward various hypotheses to account for it; some regarded it as accidental, and Stahl disregarded it altogether, as quite unimportant.

The next step of any importance in the chemical history of aeriform substances, was made by Hales, who published in 1727 his "*Vegetable Staticks*; . . . also a specimen of an attempt to analyse the air, by a great variety of chemico-statical experiments." His investigation of this subject was distinguished from those of his predecessors, chiefly by his adopting a quantitative method, and by his employing improved apparatus for preparing and collecting gases. Hales was the first to use an apparatus which was the germ of the pneumatic trough now employed. A globular vessel, filled with water, and inverted with its mouth under the surface of water in a large pan, served for the collection of the gas, which was generated in a retort, with a long neck extending up into the globular vessel serving as a receiver. The various aeriform substances he obtained, were examined only as to their inflammability, or their power of supporting combustion. He first observed the diminution of volume of atmospheric air, when mixed with nitric oxide, which afterwards, in the hands of Cavendish and Priestley afforded, such important results; but generally, Hales' experiments contributed little to the existing knowledge of aeriform substances, and he appears to have regarded the different substances of this kind which he obtained, as mere modifications of atmospheric air. His own conclusion from these "experiments, which show in how great proportion air is wrought into the composition of animal, vegetable, and mineral substances, and withal, how readily it resumes its elastic state, when, in the dissolution of those substances, it is disengaged from them," was in the following words: "Since, then, air is found so manifestly to abound in almost all natural bodies; since we find it so operative and active a principle in every chemical operation; since its constituent parts are of so durable a nature, that the most violent action of fire or fermentation cannot induce such an alteration of its texture, as thereby to disqualify it from resuming, either by means of fire or fermentation, its former elastic state; unless in the case of vitrification, when, with the vegetable salt and nitre in which it is incorporated, it may perhaps, some of it, with other chemical principles, be immutably fixed; since, then, this is the case, may we not with good reason adopt this now fixed, now volatile Proteus, among the chemical principles, and that a very active one, as well as acid sulphur, notwithstanding it has hitherto been overlooked and rejected by chemists as no way entitled to that denomination?"

Hales' main result, therefore, like many more of the results of scientific labours at that period, consisted more in the proposition of a problem than in its solution, either wholly or in part; and in this light, the general conclusion at which he arrived had the merit of being the first comprehensive indication of an important and fertile path of research, which before his time had been little pursued, but soon afterwards became the means of entirely remodelling chemical science.

Of the writers, contemporaneous with and immediately following Hales, little need be said, as their treatment of the subjects of aeriform substances, combustion, &c., was mostly argumentative and prolix rather than experimental, without adding anything to the existing state of knowledge. Thus, for instance, a lengthy section of Boerhaave's "*Elementa Chemicæ*," 1732, was devoted to criticisms of opinions and speculations as to the nature of air as an element. But by this time the speculative vein of chemical study had pretty well run out; the establishment of the phlogistic theory served to give a more systematic and comprehensive character to the science, and admitted of its being cultivated in a manner more calculated to secure progress than the desultory inquiries hitherto undertaken, under the influence either of alchemistic or of metaphysical doctrines.

Chief among the achievements of this epoch was the investigation of the difference between caustic and mild alkalis by Black, and the consequent demonstration of the existence of carbonic acid gas, or as he termed it, fixed air, this being the first instance of a gas being proved to be essentially distinct from atmospheric air.

This investigation is, perhaps, the most remarkable in the whole history of chemistry, whether it be considered in regard to its special character, or to its subsequent influence on the development of the science. Undertaken, in the first instance, merely to furnish

subject-matter for a medical thesis, it nevertheless stands out far above any other chemical research of that or any previous period; pre-eminent in its completeness and accuracy, it served as the inauguration of pneumatic chemistry, as the first decided step in that path of research which had been suggested by Hales, and as the corner-stone of modern chemistry.

Having, in the first instance, ascertained that caustic lime, exposed for some time to the atmosphere, became heavier, at the same time that it lost its causticity, instead of becoming lighter, as might have been expected if that change were really due to the escape of a ponderable heat-substance, Black perceived in this fact sufficient ground for rejecting the received doctrine of ponderable caloric. He next ascertained that the loss of causticity and the increase of weight were accompanied by a considerable absorption of air. On extending his observations to magnesia, he found that it effervesced with acids, that it lost weight by ignition, and then no longer effervesced with acids, though it still yielded the same salts with acids, as the magnesia that had not been ignited. He then sought to ascertain what was separated from magnesia by ignition, causing the loss of weight; and, with that view, heated a weighed quantity in a retort. Some water was thus obtained, but not sufficient to account for the whole loss of weight by the magnesia. This led him to suspect that air was disengaged from the magnesia by ignition; and to determine this point, he dissolved a known quantity of ignited magnesia in sulphuric acid, then precipitated it by means of a mild alkali (carbonate of potash), and found that it had increased in weight as much as the magnesia had lost in weight by ignition, and that it had recovered all the qualities which the magnesia lost by ignition. Hence he concluded that the loss of weight and alteration of qualities presented by magnesia on ignition, were due to the separation of air, and that the restitution of those qualities, and the increase of weight, when ignited magnesia was dissolved by acid and precipitated by a mild alkali, were due to its recovering from the alkali the air that had been expelled by ignition: in this latter conclusion he was guided by Hales's observation, that fixed alkali contained abundance of air. His own statement of these conclusions is very simple and clear. "*Quid ergo magnesia hoc experimento amisit, quid demum recuperavit, quod, quum addesset, tam multas qualitates dabat, cum abesset, tollebat? Aërem forte: experimenti enim vigesimi consideratione, verisimile admodum videtur, ponderis, ustione amissi, partem maximam aëre evanido constare: et hoc quidem corroboratur, quod aërem nullam, post ustionem, in acido injecta emittat. Nonne etiam verisimile, aërem iterum magnesiæ ab alkali restitui, quo tempore illam hoc de acido depellebat: alkali fixum aëre certe abundare, ex ingeniosi Hales experimentis constat, cujus quidem magnam vim eructat, ubi acido puro conjungitur; hac occasione, quamvis non puro, acido tamen certe conjungitur, et sal etiam medius ex horum conjunctione fit, copia, dotibus, omni denique modo idem, ac si acidum purum additum fuisset; sed neque tamen vel minimum aëris erumpit; nonne igitur ex alkali ab acido excutitur, et magnesiæ sese unit aër?*"—*Dissert. med. inaug. de Humore acido a cibis orto, et magnesia alba*, 1754, p. 37.

Black then examined the air evolved from magnesia and alkalis by means of acids, and found that it was identical with that given off in fermentation. He gave it the name of fixed air, and explained the difference between caustic and mild alkalis and alkaline earths as being due to the presence or absence of this substance. He showed that fixed air was essentially distinct from atmospheric air, in regard to its chemical character, and in regard to respiration and combustion; that it was produced by the combustion of fuel and by respiration, its chief characteristic being the power of combining with caustic alkalis, and to some extent neutralising them after the manner of an acid.

In his inaugural dissertation, published in 1754, he also suggested that the explosion of fulminating gold might be due to its containing air in a fixed state, and that the increase of weight observed when metals were dissolved by an acid and then precipitated by an alkali, might also be due to air furnished by the alkali.

Shortly afterwards Macbride published his *Experimental Essays* (1764), in which he gave the results of a more minute examination of the conditions under which fixed air or carbonic acid is produced in fermentation, putrefaction, &c.

Pneumatic chemistry received a further important development at the hands of Cavendish, who published in 1766 his "*Experiments on Factitious Air*" in which he gave the results of his examination of fixed air (carbonic acid) and inflammable air (hydrogen), describing their physical and chemical characters, mode of preparation, and the apparatus by which they were to be submitted to experiment. He showed that hydrogen, mixed with various proportions of atmospheric air, exploded with different degrees of violence; that equal weights of different metals gave different quantities of hydrogen with dilute sulphuric acid; that the concentrated acid did not furnish hydrogen with metals, and that when they were heated with it, another gas (sulphurous acid) was evolved.

Fixed air (carbonic acid) was shown by Cavendish to precipitate lime and magnesia from their solution in water, and again to redissolve these precipitates; he connected



with this fact the precipitation of earthy carbonates from water when boiled, and showed that potash combined with fixed air, producing a more easily crystallisable salt. He also made some advance towards the determination of the quantitative composition of the earthy and alkaline carbonates.

In 1769, Lane showed that chalybeate water contained fixed air as the solvent of the iron; in 1771, Priestley observed that fixed air kept in contact with growing plants, acquired the capability of supporting combustion and respiration, and that this change was effected only in daylight; in 1774, Bergmann published a long memoir on carbonic acid, under the name of *Acidum aëreum*, showing its existence in the atmosphere, that in its chemical functions it possessed the characters of an acid, and, in short, developing more minutely many of the details of its history, which had been previously more or less incompletely made known. Lavoisier's description of this gas, published in his *Opuscules Physiques et Chymiques* (1774), was simply a confirmation of Black's experiments.

Shortly before this time (1772), a very important discovery with regard to the constitution of the atmosphere was made by Rutherford, who showed that, in respiration, air was not, as Hales had supposed, rendered unfit for supporting combustion or respiration, by being impregnated with admixtures, but that it naturally contained a substance (nitrogen) which was incapable of supporting combustion or respiration. He obtained nitrogen by absorbing the carbonic acid from air which animals had breathed, and showed that it extinguished flame and was suffocating. In the same year, the calcination of metals again became the subject of inquiry by Priestley and Lavoisier. The former referred, in his "Observations on different kinds of Air," to the absorption of air when lead or tin was calcined in closed vessels; but, under the influence of the phlogistic theory, he failed to connect this fact with the augmentation of weight of the calces. Lavoisier, in the same year, communicated to the Académie, as the result of his experiments, his opinion, that in the calcination of metals, as well as in the combustion of phosphorus and sulphur, the increase of weight that took place was due to the absorption of air, which was again liberated in the gaseous state when metallic calces were reduced. In 1774, he made known the experiments upon which this opinion was based. One was essentially a repetition of Boyle's experiment with lead; but Lavoisier determined the weight of the retort and its contents before opening it, and thus ascertained how much air entered the retort when it was opened. This quantity was found to be exactly as much as the increase of weight in the calcined metal. In the same work (*Opuscules*), Lavoisier also showed that the augmentation of weight taking place when mercury or iron was dissolved by acids and precipitated by lime, was probably due to the combination of the metals with a gas derived from the precipitant, and although the experiments on which he based this conclusion were mixed up with the production of metallic carbonates, as well as mere oxides, the evidence they furnished of the part played by gaseous substances in chemical changes was not less important than if they had referred only to the production of true calces or oxides in the wet way. These experiments were, both in their form and significance, an exact extension of those by which Black arrived at a knowledge of the chemical nature of alkalis and their carbonates.

In the same year, Bayen showed that oxide of mercury was decomposed by heat, without any addition of phlogistic substance, that a gas was evolved in the process, and that the reduced mercury weighed less than the oxide from which it was obtained. To Priestley, however, belongs the honour of the discovery of oxygen, and of recognising its distinct nature, in August, 1774. He had, indeed, obtained it in 1771 from nitre, as Hales had obtained it in 1727 from red lead, but in both cases its true nature does not appear to have been noticed. It is, however, more questionable to whom is to be ascribed the credit of having first arrived at the conclusion that the oxygen which Priestley obtained from oxide of mercury and from red lead, was that gaseous constituent of the atmosphere which was active in the phenomena of combustion, calcination of metals, and respiration. It is at least certain that Priestley communicated to Lavoisier his discovery of oxygen very shortly after making it; but considering how much further advanced Lavoisier was at that time, in true appreciation of the phenomena with which this gas was so closely connected, than Priestley was, there seems but narrow ground for imputing to Lavoisier unfairness towards Priestley in claiming to be, jointly with him, a discoverer of oxygen.

In November, 1774, Lavoisier, in his memoir "Sur la calcination de l'étain dans les vaisseaux fermés," first put forward the opinion that atmospheric air consisted of two gases, but he did not express any decided view with regard to the nature of these gases, except that one was capable of supporting combustion and respiration, while the other could not. It was not until the end of 1775, in his memoir "Sur la nature du principe qui se combine avec les métaux pendant leur calcination," that Lavoisier stated his conclusion that the gas obtained from oxide of mercury by heat, was the

same as the constituent of atmospheric air which supported combustion and respiration, and combined with metals in calcination. In this memoir, he made known his view of the composition of carbonic acid, which he showed was formed when oxide of mercury was heated with carbon, and was therefore to be regarded as a compound of carbon with that constituent of atmospheric air which supported combustion.

Scheele's investigation on the constitution of the atmosphere,—made in 1774-75, but not published until 1777, in his essay on "Air and Fire,"—comprised another independent discovery of oxygen gas, obtained by heating nitre or metallic oxides, but as he was content with the fact, there was no dispute as to the priority of the discovery. This essay also contained many valuable results connected with the composition of the atmosphere, the phenomena of combustion, and other details relating to pneumatic chemistry, especially the quantitative composition of the atmosphere, which, since the discovery of its nature, had been a more definite object of investigation than it had formerly been. As contributors to the attainment of this result, were Fontana, Landriani, Lavoisier, Ingenhous, Sigaud de la Fond and Davidson. It was, however, by Cavendish's "Experiments on Air," published in 1784-86, that the true quantitative composition of the atmosphere was first established, and the cause of the discrepancies which had been observed in eudiometrical experiments made known.

In the early part of 1783, which was a period of great importance in the history of chemistry, the knowledge of æiform substances had made very considerable progress, so far as concerned the establishment of facts as to the existence of different gases, the part played by atmospheric air in combustion and respiration, and by gaseous substances generally in most chemical phenomena. A passage in the "*Histoire de l'Académie Roy. des Sciences*," for 1776, published in 1779, will serve to show the change which had taken place with regard to this subject. "Les substances aëriformes sur lesquelles nous n'avions que des observations isolées, sont devenues, depuis quelques années, l'objet des recherches des chimistes; et elles ont jeté un grand désordre dans les théories les mieux établies et les plus fermement adoptées. En effet, on a reconnu que ces substances, qui, au degré de chaleur de l'atmosphère, sont dans l'état de fluides expansibles, entroient dans la composition de la plupart des corps solides et fluides; c'étoit donc un nouvel ordre de substances auxquelles il falloit avoir égard dans l'analyse de ces corps." In the same volume, the increase of weight in calcination of metals was also referred to: "Ainsi l'on a observé dans les calcinations des métaux, et leur réduction, que l'explication de Stael n'étoit suffisante; que les substances métalliques s'unissoient, par la calcination, avec une espèce d'air, qui s'en dégageoit ensuite dans leur réduction," while not longer back than 1766, the same subject was referred to in the "*Histoire de l'Académie*" for 1763, in the notice of a memoir by Hellot, Tillet, and Macquer, "Sur les Essais des Matières d'Or et d'Argent," in very different terms: "L'augmentation observée dans le bouton d'argent fin n'est . . . qu'apparente, et il ne se fait aucune transmutation du plomb en argent; mais ce premier métal, qui sembleroit devoir considérablement diminuer de poids par l'action du feu et par les fumées continuelles qu'il exhale en se convertissant en litharge, augmente au contraire de poids. . . . Le fait n'est point équivoque, . . . et c'est un vrai paradoxe chymique, que l'expérience met cependant hors de doute. Mais s'il est facile de constater ce fait, il ne l'est pas autant d'en rendre une raison satisfaisante; il échappe à toutes les idées physiques que nous avons, et ce n'est que du temps, qu'on peut attendre la solution de cette difficulté." Tillet, who had studied this fact very carefully, remarks in his memoir, "Nous sommes donc forcés de convenir que cette augmentation de poids étant constante et bien décidée . . . devient par là le sujet d'une recherche curieuse, s'il est possible de saisir un point de physique aussi délicat."

Besides the gases already mentioned, Priestley had discovered hydrochloric acid gas, ammonia, fluoallic gas, sulphurous acid, and nitrous oxide. He had also devised the use of mercury in place of water for the pneumatic trough. Scheele had discovered chlorine. Volta had pointed out, in 1776, the peculiarity of the inflammable air of marshes, in yielding carbonic acid when burnt, and had made a comparative examination of it and other inflammable gases, as regarded the proportions of oxygen requisite for their combustion. He also showed that a mixture of atmospheric air and inflammable air could be exploded by the electric spark, and Kirwan had endeavoured, in support of the phlogistic theory, to identify phlogiston with the inflammable air obtained by dissolving metals with dilute acids. But, in general, there was an absence of any connected interpretation of the facts which had been ascertained. Lavoisier had given, in his *Opusculs*, a comprehensive historical statement of the views which had been entertained with regard to æiform substances, and at the same time put forward his own views with regard to combustion. In his paper on the combustion of diamond, phosphorus, and organic substances, he showed that only a part of the



atmospheric air was concerned in the process, and that fixed air was the only gas remaining after the combustion of organic substances when vital air was substituted for atmospheric air. He showed that sulphuric acid contained vital air and sulphur; that the production of a salt by the exposure of pyrites to the atmosphere, consisted in a simultaneous absorption of the same air by the sulphur and iron; that nitric acid contained this air; and that phosphorus was convertible into phosphoric acid by nitric acid. In 1781, he published an approximate analysis of carbonic acid, and showed that it, in common with all other acids as he maintained, contained oxygen. His attempts, in 1782, to explain the precipitation of one metal by another, as consisting in a transfer of oxygen from one to the other, in opposition to Bergmann's view, that it consisted in a transfer of phlogiston, were less successful than some of his other investigations; and just at this time his attention was directed to an objection urged against his views, that they did not account for the evolution of hydrogen when metals were dissolved by dilute acids, nor explain whence they derived the oxygen, which he maintained it was necessary they should combine with, to form oxides, before they could form salts with the acids.

About the end of 1781, Cavendish commenced some experiments, which "were made principally with a view to find out the cause of the diminution which common air is well known to suffer, by all the various ways in which it is phlogisticated, and to discover what becomes of the air thus lost or condensed" (*Phil. Trans.*, 1783, p. 119): "Having now mentioned the unsuccessful attempts I made to find out what becomes of the air lost by phlogistication, I proceed to some experiments which serve really to explain the matter. In Dr. Priestley's last volume of experiments, is related an experiment of Mr. Warltire's, in which it is said, that on firing a mixture of common and inflammable air by electricity . . . in glass vessels, the inside of the glass, though clean and dry before, immediately became dewy; which confirmed an opinion he had long entertained, that common air deposits moisture by phlogistication" (*ibid.* p. 126). In studying this fact, Cavendish met with a difficulty, consisting in the production of an acid in some instances; and the examination of the conditions under which this took place delayed the publication of his experiments until 1783; but so early as the summer of 1781, he had ascertained that, "when a mixture of inflammable and dephlogisticated air is exploded in such proportions that the burnt (i.e. residual) air is not much phlogisticated, the condensed liquor contains a little acid, which is always of the nitrous kind, whatever substance the dephlogisticated air is procured from; but if the proportions be such that the burnt air is almost entirely phlogisticated, the condensed liquor is not at all acid, but seems pure water, without any addition whatever; and as, when they are mixed in that proportion, very little air remains after the explosion, almost the whole being condensed, it follows that almost the whole of the inflammable and dephlogisticated air is converted into pure water." The weight of the water so produced was also shown to be equal to the joint weight of the two gases. Cavendish adds, "Last summer (1783), a friend of mine gave some account of these experiments to M. Lavoisier, as well as of the conclusion drawn from them, that dephlogisticated air is only water deprived of its phlogiston."

These experiments, which furnished evidence of the compound nature of water—the only point that was wanting to render Lavoisier's theory complete, and to overthrow the phlogistic theory—were interpreted by Cavendish in perfect accordance with older views, to which he uniformly adhered. The water obtained by exploding a mixture of inflammable and dephlogisticated air, was never regarded by him as the result of a chemical combination of two distinct substances, but, strictly in accordance with the spirit of the phlogistic theory, merely as being the result of a mutual and compensating alteration of the two kinds of air, both of which he supposed to be, at the same time, equally air and also equally water, the difference between the two kinds of air, and between either of them and water, consisting solely in their condition with regard to the unknown principle, phlogiston. His own language in reference to this point is so clear and explicit, that it is remarkable this fact should have been entirely overlooked in the long controversy which has been maintained as to the discovery of the compound nature of water, or the originator of the view that water is a compound of the two gases.

It is somewhat questionable what was the exact nature of Cavendish's views with regard to phlogiston; so far as may be inferred from his writings, he appears to have regarded it as imponderable. Certainly he did not, as has been frequently asserted, regard hydrogen as phlogiston; and, though he mentions that opinion, as put forward by Kirwan and Priestley, he expressly states his dissent from it. With regard to his view of the nature of dephlogisticated and inflammable air, however, there is no room for doubt or uncertainty:—"dephlogisticated air is only water deprived of its phlogiston," and inflammable air "is either phlogisticated water or else pure phlogiston, but in all probability the former" (*Phil. Trans.* 1784, p. 140). Again, after discuss-



ing the probable source of the acid produced in some of his experiments, he says:—"We must allow that dephlogisticated air is, in reality, nothing but dephlogisticated water, or water deprived of its phlogiston; or, in other words, that water consists of dephlogisticated air united to phlogiston; and that inflammable air is either pure phlogiston . . . or else water united to phlogiston, since, according to this supposition, these two substances united together form pure water." His account of the nature of phlogistication of pure air renders his opinion still more clear: "adding dephlogisticated air to a body is equivalent to depriving it of phlogiston, and adding water to it." "In the detonation of nitre with inflammable substances, the acid unites to phlogiston and forms phlogisticated air" (nitrogen); but in the production of nitric acid from a mixture of oxygen and nitrogen, "the reverse of this process was carried on, namely, the phlogisticated air united to the dephlogisticated air, which is equivalent to its being deprived of its phlogiston, and was reduced to nitrous acid" (Phil. Trans. 1785, p. 380). As illustrative of this process he mentions the oxidation of mercury in his first paper, and, even in 1785, the formation of nitric acid. He had formerly come to the conclusion that phlogisticated air (nitrogen) was "nothing else than nitrous acid united to phlogiston. According to this conclusion, phlogisticated air ought to be reduced to nitrous acid by being deprived of its phlogiston. But as dephlogisticated air is only water deprived of its phlogiston, . . . therefore phlogisticated air ought also to be reduced to nitrous acid by being made to unite to, or form a chemical combination with, dephlogisticated air, only the acid formed this way will be more dilute than if the phlogisticated air was simply deprived of its phlogiston" (Phil. Trans. 1785, p. 379). This assumed dilution of the acid shows that he considered water to be produced by the transfer of phlogiston from nitrogen to oxygen, as well as by the transfer of phlogiston from hydrogen to oxygen, just as he considered it to be produced also, by the transfer of phlogiston from mercury to oxygen, and to remain as a constituent of the oxide of mercury.

The argument that Cavendish regarded water as a compound, rests solely upon the assumption that he considered inflammable air to be phlogiston, an assumption not only quite gratuitous, but directly opposed to his own statements as to this point. "I know of no experiment," he says, "which shows inflammable air to be pure phlogiston, rather than a union of it with water, unless it be Dr. Priestley's experiment of expelling inflammable air from iron by heat alone;" and, he adds, it is "more likely that the inflammable air was formed by the union of the phlogiston of the iron filings with the water dispersed among them" (Phil. Trans. 1784, p. 137). Even the fact that the water, produced by exploding a mixture of inflammable and dephlogisticated air, was equal to the joint weight of the two gases, was not interpreted by Cavendish as indicating the formation of a compound, according to present ideas, but merely as showing that both kinds of air were, as he expresses it, "turned into water." The change, in his estimation, was of much such a nature as that in the production of water by mixing ice and steam; or in the contact of a negatively electric body with another positively electric. He even expressed his dissent from Lavoisier's view of the fact, while admitting that it could be as well expressed according to that view, as according to the phlogistic theory; and he speaks of Lavoisier's view as an "hypothesis," according to which "we must suppose that water consists of inflammable air united to dephlogisticated air." The difference between Cavendish's real view and this expression of Lavoisier's, will appear trivial or nothing if they are considered in the manner which has now become habitual; but the fact that Cavendish took the pains to refer to the difference between his view and that of Lavoisier, is sufficient proof that, in his own estimation, the difference was not slight; and if the tendencies and spirit of the phlogistic theory are fairly considered, it will be evident even now that it was no slight difference.

It is only to the disregard of the point of view from which this and similar phenomena were considered, according to the phlogistic theory, that the spurious argument and signal misconception, characteristic of much of the water controversy, can be ascribed—misconception so great, that the late Dr. Wilson, in his biography, has asserted it to be "undeniable" that Cavendish considered every oxidisable body contained hydrogen! "Inconceivable" would be a more correct term to apply to the notion that any such opinion was ever thought of by Cavendish, and more consistent with that high estimation of his philosophical character which has always been so generally entertained, and which rests on so solid a foundation. It is only by such a disregard of the phlogistic point of view, that it is possible to account for the attempt to claim for Cavendish any further share in the discovery of the composition of water, than that of having been the first to recognise the fact that it was the sole product of the explosion of oxygen and hydrogen in certain proportions: with regard to this having been done by Cavendish it seems hardly possible that there should be any dispute. It is equally impossible to perceive any ground for the assertion that he did anything

more than supply the evidence of the composition of water, without, however, forming any conception of its compound nature, or, in other words, adopting the true interpretation of his experimental results. If the mere recognition of the fact that hydrogen and oxygen yielded water by explosion, be held to constitute the discovery of its composition, both Warltire and Priestley should be allowed to participate in the credit of having made it, and, to some extent also, Macquer and De la Méthérie, who, in 1776, had observed that water was the product of combustion of inflammable air. But the view that water was a compound, was incompatible with the system of chemical philosophy then prevailing, and was, in fact, the means of subverting it. The credit of having first given the true interpretation of the facts observed by Cavendish, is certainly due to Lavoisier; and to that extent he may be regarded as the discoverer of the composition of water, inasmuch as the advancement of chemical science, at that time, and in this case especially, consisted more essentially in the correct interpretation of known facts, than in the observation of new facts.

It would be improper not to mention here the claim which has been made for James Watt, as having been the discoverer of the composition of water, a claim which appears to involve a disregard of what really constitutes a title to be considered as a discoverer. Watt certainly was the first to put forward, in 1783, the opinion that water was a compound of inflammable and dephlogisticated air; but that opinion was merely an hypothesis, based upon data furnished to him by Priestley, and unsupported by any experimental observation of his own. In fact, he never appears to have laid claim to anything more than having put forward this view as a speculation; and though, for a time, he believed he had been unfairly treated, his only complaint was that his "ideas" had been pirated, and that no mention had been made of his "theory," either by Cavendish or Lavoisier, to whom it had been communicated.

The communication of Cavendish's results to Lavoisier, by Blagden in 1783, appears to have been received by him with doubt as to their accuracy. The combustion of inflammable air had already occupied his attention, about the end of 1781, under the belief that, like sulphur and phosphorus, it would yield an acid. In his memoir on this subject, read in 1783, he says, "*L'analogie m'avoit porté invinciblement à conclure que la combustion de l'air inflammable devoit également produire un acide.*" At the time of Blagden's communication, however, the evolution of hydrogen when metals were dissolved by dilute acids, and the reduction of metallic oxides by inflammable air, were inexplicable according to Lavoisier's views; and he appears to have thought Cavendish's experiment sufficiently important to repeat it. The result which he obtained, at once showed him that his preconceived opinion as to the combustion of inflammable air was wrong, and it furnished him with the key to the explanation of those difficulties which were then being urged against the correctness of his views by Kirwan and other supporters of the phlogistic theory. He followed up the subject by decomposing water, and contributed to establishing its quantitative composition. Berthollet and other chemists soon afterwards adopted his views; before the end of the 18th century the antiphlogistic theory was generally established; and with its establishment, the chemical importance of gaseous substances was fully recognised.

Since that time, the knowledge of the chemical and physical characters of gases has been largely extended by the investigations of numerous chemists. The relations of volume obtaining in the combination of gases, first definitely pointed out by Gay-Lussac and Humboldt in 1805, and subsequently developed by the former in 1809, have but recently been fully brought to bear upon the theory of chemical constitution, and, like the phenomena of diffusion investigated by Dalton and Graham, belong so entirely to the chemistry of the present time, that they will require to be treated in separate articles.

B. H. P.

**GAS BURNERS AND FURNACES.** The forms of gas-burner used for illumination, are described in *Ure's Dictionary of Arts, Manufactures, and Mines*, art. COAL-GAS, i. 733. In these burners, the main condition to be fulfilled is, to supply the flame with just so much air as to burn the whole of the hydrogen in the gas, and a sufficient quantity of the carbon to prevent the formation of visible smoke, but, at the same time, to separate a certain quantity of the carbon within the flame in the form of minute solid particles, which, being rendered incandescent by the flame, impart to it a high degree of luminosity; perfect combustion is not desirable, as all the products would then be gaseous, and very little light would be emitted. (See COMBUSTION, i. 1094, and FLAME, ii. 654.) But when coal-gas is used as a source of heat, it is desirable to make the combustion as complete as possible, as this condition insures the production of a high temperature and the absence of smoke. This object is attained by mixing the combustible gas, before it reaches the burning point, with the quantity of air required to burn it completely. A simple and effective contrivance for this purpose is to fix on the top of the chimney of an ordinary argand gas-burner a piece of wire-gauze, then turn on the gas, and light it above the gauze. The gas then becomes

mixed with air in passing up the chimney, and this mixture, when set on fire above the wire-gauze, burns with a pale blue, perfectly smokeless flame, producing a very intense heat, and well adapted for heating basins, small crucibles, or other vessels. If the wire-gauze is of the proper degree of fineness, and fits closely on to the top of the chimney, the flame will not extend to the mixture of air and gas below the wire-gauze, because in passing through the meshes, it would be cooled below the burning temperature, as in the miner's safety-lamp (i. 1101).

But the form of gas-burner now most generally used in chemical laboratories, as a source of heat, is that contrived by Professor Bunsen, and represented in *fig. 496*. The gas, supplied by a flexible tube attached at *t*, passes through a set of small holes into the box *a*, in which it mixes with atmospheric air entering freely by a number of holes as shown in the figure. The gaseous mixture passes up the tube *b*, and is inflamed at the top, where it burns with a single tall blue flame, which gives no smoke and very little light, but much heat. The flame may be made large or small at pleasure by regulating the supply of gas; and by arranging two or more such tubes, together with an air-box containing a sufficient number of holes, a very powerful burner may be constructed.

This form of burner is, however, subject to two defects; sometimes the flame burns white and smoky, and sometimes it blows down, the gaseous mixture exploding, and the gas then burning with a smoky flame in the air-box *a*. The remedies for these defects are as follows:—If the flame is white only when the gas is turned on very full, the remedy is to lessen the supply of gas; but if the flame continues to burn white at the top, when the gas is gradually turned off and the mass of flame slowly sinks, then the holes which deliver the gas from the supply pipe into the air-box are too large, and are placed too directly under the centre of the vertical tube *b*: these defects must be corrected in the instrument. Finally, when the flame blows down, it is because the supply of atmospheric air is too large in proportion to the supply of gas, and their relative proportions must be altered. To effect this alteration, Mr. Griffin (to whose kindness the editor is indebted for the following descriptions of gas burners and furnaces) places over the air-box *a* a thin brass cap, *c*, perforated with holes, and capable of turning round so as partially to close the holes, and thus lessen the supply of air. If, when the gas is alight, the flame needs to be lowered, first the supply of air is to be lessened, then the supply of gas. If the flame is to be enlarged, first the supply of gas must be increased, and then the supply of air. In short, to prevent the flame blowing down, the gas must always be first placed in excess, and then have the proper quantity of air adjusted to suit it, by means of the regulator *c*.

To produce a spreading flame, and render the burner better adapted for heating an evaporating basin, Mr. Griffin places over the mouth of the vertical tube *b* (*fig. 496*), a flat cast-iron box, *d*, with many holes round its margin, and a few small ones on the top. The flame thus produced consists of a series of radiating jets, forming a horizontal circular flame. *Fig. 497* represents a variety of this rose burner in which the head is not removable, but the efflux of the mixed gases is regulated by a sliding valve *b*. When the slide is pushed over the central hole, the burner gives a number of small flames in a circle suitable for boiling and evaporation; when it is pushed aside, the burner gives a single tall flame adapted for ignition and fusion.

**Gas Furnaces.** The power of the burner just described, and, indeed, of every kind of gas-burner, may be greatly increased by surrounding the flame with a jacket of fire-clay, or some other substance of small conducting power, which will prevent the dissipation of the heat by radiation. In this manner gas furnaces may be constructed capable of producing very high temperatures with but a small expenditure of gas.

*Fig. 498* represents a gas furnace arranged for boiling and evaporation. *a* is the gas burner, like that represented in *fig. 496*: it is 12 inches high, the bore of the tube *d* is 1 inch, and the diameter of the fire-box *c* is 4 inches: *b* is an iron stool with three legs; *c*, a furnace-body, or iron jacket, lined with plumbago or fire-clay. *Fig. 499* shows the jacket and lining in section, and marks the position of the fire-box, *c*, of the gas-burner. This furnace is 14 inches high and 9 inches in diameter. The three

Fig. 496.

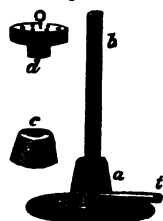
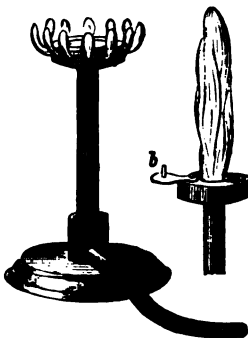


Fig. 497.





brackets fixed on the upper part of the jacket serve to support the vessel containing the liquid to be boiled or evaporated. A porcelain basin 16 or 18 inches in diameter can be thus supported. It is important to allow, between the jacket *c* and the evaporating basin, plenty of space for the escape of the heated air which ascends from the interior of the furnace. When the evaporating basin is of small diameter, it may be supported on triangles placed within the furnace *c*. Round the vertical tube of the gas-burner *a*, there is in the bottom of the furnace *c* (fig. 499) a circular opening 2 inches in diameter, through which the air passes

Fig. 498.



Fig. 499.



freely, partly to feed the flame and partly to be heated by the flame, and directed upwards in a continuous current upon the lower surface of the basin that is to be heated. The flame within the furnace burns steadily. No side currents of air agitate it. No part of it touches, or must be permitted to touch, the basin, which should receive its heat solely from the mass of ascending hot air. The gas-burner thus arranged, and supplied by a gas-pipe of  $\frac{1}{4}$  inch bore, burns about 33 cubic feet of gas in an hour, and the flame which it produces, acting upon water contained in an open porcelain evaporating basin, will heat from 60° to 212° F.:

1 quart in 5 minutes | 1 gallon in 15 minutes | 2 gallons in 30 minutes

When the water boils, it is driven off in steam at the rate of more than a gallon of water per hour.

By increasing the draught and confining the heat still more, the same gas burner

Fig. 500.



may be made to give heat enough for the fusion of silicates with carbonate of soda. Fig. 500 represents a gas furnace contrived by Mr. Griffin for this purpose. *a* is the gas-burner; *b*, a tall iron stool; *c*, a chimney which collects atmospheric air to feed the flame, and leads it up close to the vertical tube of the gas-burner, by which contrivance the air is warmed and the tube cooled; *d* is a sole or plate of fire-clay; *i* is a cylinder of fire-clay, 4 inches high, and  $4\frac{1}{2}$  inches diameter; *k* is a plumbago or fire-clay furnace, in which is placed a small cast iron ring, the form of which is shown in fig. 501, and on this ring the platinum crucible is adjusted; *l* is a fire-clay or plumbago reverberatory

Fig. 501.



dome; and *g* is the chimney, 24 inches long and  $3\frac{1}{2}$  inches wide. The crucible being adjusted, the gas lighted, and the dome and chimney put on, the lapse of 12 or 15 minutes, according to the quality and pressure of the gas, suffices for the fusion of 1000 grains of carbonate of soda in a platinum crucible.\*

The crucible is placed very high above the orifice of the tube *a* at which the gas is inflamed. The distance is, in fact, about 10 inches, the point of maximum heat in the flame being at nearly that distance from the burner, more or less according to the pressure and the quality of the gas. The gas which rises from the burner *a*, though mixed with as much air as it will bear without becoming explosive when lighted, does not contain sufficient oxygen to burn all the carbon present in it. The flame produced is, consequently, quite superficial. The gaseous mixture burns only on the surface, where it is in contact with fresh atmospheric air, and it requires time to take up the requisite amount of oxygen. The draught produced by the joint action

\* If this quantity of fused carbonate of soda is permitted to cool and consolidate in a platinum crucible, the salt is liable to expand and burst the crucible.

of the two chimneys *c* and *g* carries the flame rapidly to a great height before the point of complete combustion is attained.

When the highest degree of heat is not required, the reverberatory dome *l* may be omitted. It must also be dispensed with when the crucible is to be heated is of comparatively large size, because it is then liable to lower the temperature of the furnace by impeding the draught.

Fig. 502 shows a form of the furnace adapted for igniting a large fire-clay crucible, as when oxide of copper is to be dried for use in organic analysis. The crucible is enclosed within a reverberatory dome *f*. The chimney is provided with a damper to lessen the draught when small crucibles are to be heated.

The action of these furnaces may be judged of by a peculiar roaring noise which they produce. If the gas and air are mixed in due proportions, the roar is regular and continuous. If there is too much gas, the roar is lessened; if too much air, the roar is increased, but is rendered irregular and intermittent. The greater the noise, the greater the heat in the furnace: but when the roar becomes spasmodic, the flame is on the point of blowing down. To prevent that occurrence, the proportion of air must be lessened or that of gas increased.

The effects ascribed to the various arrangements of this gas-furnace, can be produced with gas supplied by a pipe of a  $\frac{1}{4}$ -inch bore, and at a moderate pressure, giving from 30 to 40 cubic feet per hour.

The principles of heating by gas, which have led to the construction of this furnace, may be summed up as follows:—When a crucible or other solid body is to be heated, it is to be wrapped in a single flame at the point of maximum heat, and loss of heat by radiation and conduction is to be prevented by the interposition of non-conducting materials (plumbago or fire-clay); and when liquids are to be boiled or evaporated, particularly when they are contained in vessels of glass or porcelain, the flame is to be broken up into numerous horizontal jets, and these are to be made to supply a large and regular current of highly heated air, by which alone, and not by the direct application of the flame, the vessel containing the liquid is to be heated. In both cases, provision must be made to secure a sufficient draught of air through the furnace, because every cubic foot of gas requires for combustion 10 or 12 cubic feet of air, and the gases which have done their duty must be rapidly carried away from the focus of heat. If the steam, the carbonic acid gas, and the free nitrogen, which constitute the used-up gases, are not promptly expelled, fresh gaseous mixture, in the act of producing additional heat by combustion, cannot get near the object that is to be heated, and the heat so produced out of place is wasted.

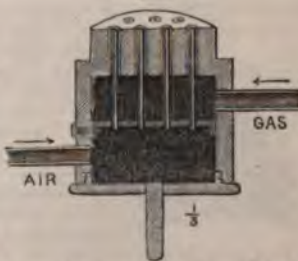
**Griffin's Blast Gas Furnace.** This is a more powerful apparatus adapted for metallurgic operations, such as fusing considerable masses of metal, assaying, roasting, &c. It consists of two parts: first, of a particular form of gas-burner, which is supplied with gas at the usual pressure, and with a blast of common air, supplied by bellows or a blowing machine, at about ten times the pressure at which the gas is supplied; and secondly, of a furnace, which is built up in a particular manner, round the flame produced by the gas-burner, and the crucible exposed to ignition. The object of this particular construction is to accumulate and concentrate in a focus the heat produced by the gas flame, and to make it expend its entire power upon any object placed in that focus. This apparatus can be made of various sizes, according to the amount of work required from it.

The gas-burner is a cylindrical iron reservoir, shown in section in fig. 503, which is drawn on a scale of one-third the full size. It contains two chambers, not in communication with one another. Into the upper chamber, gas is allowed to pass by the tube marked GAS. Into the lower chamber, air is forced by the tube marked AIR. The upper part of the burner is an inch thick in the metal. Through this solid roof, holes from 6 to 26 in number are bored for the escape of the gas. The number of holes, depends, of course, upon the heating power required from the burners. The air passes from the lower chamber, through

Fig. 502.



Fig. 503.





a series of metal tubes, placed in the centre of the gas-holes, and continued to the surface of the burner, so that the gas and air do not mix until both have left the gas-burner, and then a current of air is blown through the middle of each jet of gas. The bottom of the gas-burner is made to unscrew, and the division between the two chambers, which carries the air-tubes, is easily removable for the purpose of being cleaned. The gas and air pipes generally used in the inventor's experiments were both half an inch in the bore, and ten inches long; the gas had usually a pressure of half an inch of water, and the blast of air about ten times that pressure. The quantity of gas used in an hour was about 100 cubic feet. The stopcock which supplied it had a bore of half an inch. The round rod represented at the bottom of the burner, *figs.* 505, is intended to fit it to the support, shown by *b*, in *figs.* 505 and 506.

When the gas is lighted and the blast of air is put on, the flame produced by the gas-burner is quite blue, and free from smoke. It is two inches in diameter, and three inches high, and the point of greatest heat is about two inches above the flat face of the gas-burner. Above this steady blue flame there rises a flickering ragged flame, several inches in height, varying with the pressure of the gas. In the blue flame, the platinum wires fuse readily.

When the gas is burning in this manner, and the apparatus is attached to flexible tubes, the burner may be inverted or held sideways, without disturbing the force or regularity of the flame, so that the flame may be directed into a furnace at the bottom, the top, or the side, as circumstances may require.

The following articles are used in building up the gas furnace for different experiments. They vary in size according to the volume of the crucible, or the weight of the metal to be heated.

1. A circular plate of fire-clay, two inches thick, with a hole in the centre, exactly fitting the upper part of the gas-burner, which is made to enter into the hole three-quarters of an inch. In external diameter, this clay plate agrees with each size of furnace.

2. A cylinder of fire-clay, of which two pieces are required to constitute the body of each furnace. In the middle of each cylinder, a trial-hole is made, one inch in diameter, to which a fire-clay stopper is adapted.

3. A fire-clay cylinder, closed at one end, and pierced near the open end with six holes of half an inch in diameter. The thickness of the clay is immaterial. This cylinder is three inches high and three inches in diameter.

4. A circular plate of fire-clay, two and a half inches or three inches in diameter, and one inch thick. Similar pieces  $\frac{1}{2}$  inch thick are useful.

5. A cylinder of plumbago, to be used as a crucible support. It is three inches in inside diameter, one inch in height, and pierced with twelve holes of three-eighths of an inch bore.

6. A similar cylinder of plumbago, two or three inches high, pierced with 24 holes of three-eighths of an inch bore.

7. A thin plate of plumbago, three inches in diameter, viz. of the same diameter as the cylinders 5 and 6. It has a small hole in the middle, and being of soft material, the hole can be easily cut or filed to suit crucibles of any desired size.

To suit the larger kind of crucibles and furnaces, cylinders are made resembling the above in form, but of greater diameter.

As in all cases the heating power of the gas furnace spreads laterally and does not rise vertically, the most advisable form of the crucibles required for use in it, is *short and broad*, not tall and narrow, and the supporting cylinders must be shaped accordingly. No fire-bars or grates must be used to support the crucibles in this gas furnace, because no material formed into narrow bars can sufficiently withstand its power of fusion and combustion.

8. A plumbago cylinder, or crucible-jacket, two and a half inches high, two and a half inches in diameter, and a quarter of an inch thick in the walls. It has six holes of three-eighths of an inch diameter near one end.

9. A circular cover or dome (*fig.* 504) flanged at the bottom, and having a knob or handle at the top. It is pierced with 24 holes of a quarter of an inch in diameter, arranged in two rows near the bottom. This dome, when of small size, is made of plumbago; when large, of fire-clay.



*Fig.* 504.

10. Plumbago crucibles made with a solid overhanging rim, the use of which is to suspend the crucibles over the gas-burner, by means of the cylinders, Nos. 5 and 6. When the crucibles are too small to fit the cylinders, the flat plate, No. 7, is filed to fit the crucible, and is then placed on the cylinder, to whose diameter it is adapted.

Besides these pieces of fire-clay and plumbago, it is necessary to be provided with a strong iron tripod, to sustain the furnace, as represented by *c*, in *figs.* 505, 506; and



iron pan, in which to place the furnace; and a quantity of gravel, or rounded flints, not less than half an inch, nor more than one inch in diameter. These pebbles form an essential part of the gas-furnace.

*Gas-furnace heated at the top, exhibited in section by Fig. 505.*—*a* is the gas-burner, (fig. 503); *b* is the support for it, when used below the furnace; *c* is the iron tripod support for the furnace; *d, d'*, are two perforated clay plates, like No. 1, adapted to the gas-burner *a*; *e, e*, are two clay cylinders, like No. 2. These pieces *a* to *e*, are similar in all the furnaces represented by figs. 505 and 506.

The interior of the furnace is built up as follows:—The clay plate *d*, is put upon the tripod *c*. Over the central hole in *d*, the clay cylinder (No. 3) is placed, and upon that cylinder two or three of the clay plates (No. 4). Upon these a porcelain or platinum crucible is placed. If it is of platinum, a piece of platinum foil may be put between the crucible and the uppermost clay plate, to protect the crucible from contact with particles of iron, or against fusion with the clay. The crucible is to be covered by the plumbago jacket (No. 8). The space between this pile in the centre of the furnace and the two cylinders *e, e*, which form the walls of the furnace, is to be filled with flint-stones, or gravel, washed clean and dried. The stones which answer best are rounded, water-worn pebbles, of half an inch to one inch diameter. These may be piled up to the top edge of the jacket (No. 8). The number of clay plates (No. 4) must be such as to bring the top of the crucible, to the distance of two inches, or two and a half inches at the utmost, from the flat face of the gas-burner *a*. In some cases, merely one of the furnace cylinders, *e*, is necessary, in which case the crucible and its jacket is placed directly upon the cylinder (No. 3), and when only a moderate heat is required, even the packing with pebbles may be dispensed with. Another means of diminishing the heat is to increase the distance between the gas-burner and the crucible.

The apparatus being thus arranged, the gas is to be turned on, and lighted; the blowing-machine is to be put into action; and the nozzle of the gas-burner is to be depressed into the central hole of the clay plate *d'*, as shown in fig. 505. The whole force of the blue flame then strikes the crucible; part of it forces its way through the holes in the jacket (No. 8), and part of it rises and passes over the upper edge of the jacket; after which it forces its way downwards between the pebbles. The carbonic acid gas and the vapour of water which result from the combustion of the gas, together with the nitrogen of the air, and any uncombined oxygen, accompany it. No space being left open for the escape of these gases at the upper end of the furnace, they go downwards through the interstices among the pebbles, and passing through the holes in the cylinder (No. 3), and through the central hole in the lower plate *d*, fig. 505, escape finally into the air. In this progress, the hot gases give up nearly all their heat to the flint-stones. Water and gases escape below at a very moderate temperature, water even running down in the liquid state, while the stones rapidly acquire a white heat, and if the blast and the supply of gas is continued, they retain that white heat for any desired length of time—for hours.

At the end of ten minutes after lighting the gas, the crucible, placed in the described circumstances, and exposed to the full action of the heat of the gas, and surrounded by substances which are bad conductors of heat, is raised, with the jacket and pebbles around it, to a white heat. The consequence is, that the full power of the gas jet is then exerted upon the crucible and its contents.

If it is desired to inspect the substance subjected to the action of heat in this furnace, the gas-burner is lifted out, and the crucible is examined through the hole in the clay plate. To make it possible to inspect substances at a white heat, the view is taken through a piece of dark cobalt-blue glass. If the substances submitted to heat suffer no harm from the action of oxygen, it is better to dispense with a crucible cover, and throw the jet flame directly down upon the substance to be heated. The

Fig. 505.



action is then more rapid. When the burner is taken out, the substance in the crucible can be stirred, if it is considered necessary.

The following experiment will give an idea of the power of a furnace of this description. A common clay crucible, three inches high and three inches diameter at the mouth, was filled with about twenty-four ounces of cast iron. It was mounted like *fig. 505*, in a furnace of four inches internal diameter, and eight inches deep. The pebbles were filled in to the edge of the crucible. No crucible-cover and no jacket were used. The flame was thrown directly upon the iron. In a short time the iron melted; the oxygen then converted some of the cast iron into magnetic oxide of iron, which formed a thin, infusible mass on the surface of the cast iron. At twenty minutes from the lighting of the gas, the furnace was dismantled. The crucible was taken out. A hole was broken by an iron rod in the infusible surface of oxidised iron, and the fused cast iron below it was decanted into a mould, and made a clear casting weighing twenty ounces.

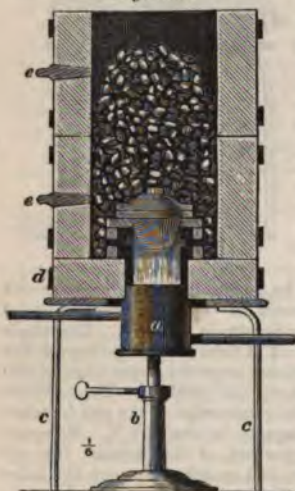
In the same small furnace 32 ounces of copper can be fused in fifteen minutes. When the furnace is hot, that quantity of copper or cast iron can be fused in ten minutes.

In a furnace of the same dimensions, but with a gas-burner having only six, instead of sixteen jets, 16 ounces of copper or of cast iron can be completely fused, in ten minutes if the furnace is cold, and in seven minutes if the furnace is hot.

These experiments show that within twenty minutes a heat is producible in this furnace, which is more than sufficient for the decomposition of silicates by fusion with the carbonates of potash, soda, or baryta.

*Gas-furnace heated at the bottom, exhibited in section by fig. 506.*—In this furnace the parts marked *a, b, c, d, e, e*, are the same as those similarly marked in *fig. 505*;

*Fig. 506.*



but the gas-burner is in this case put into the bottom of the furnace, instead of the top, and the arrangement of the crucible and its support is altered in the manner shown by the figure. Upon the centre of the clay plate *d*, the perforated plumbago cylinder and cover (Nos. 5 and 6) are placed; and upon them a flanged plumbago crucible. The size of the crucible, and the height of the perforated cylinder, are to be so adjusted that the bottom of the crucible shall be struck by the hottest part of the gas flame; that is to say, the space left between the face of the gas-burner and the bottom of the crucible must not exceed  $2\frac{1}{2}$  inches. The crucible is provided with a closely fitting cover, and pebbles are then filled in between the crucible jacket and the furnace cylinder *e*, and are covered over the crucible until both the pieces of the furnace *e, e*, are filled. The gas is then lighted, the blast of air is set on, the gas-burner is forced up into the hole in the clay plate *d*, and the operation proceeds. In from ten to twenty minutes after the gas is lighted—this difference of time depending upon the size of the furnace and the weight of the metal contained in the crucible—the interior of the lower cylinder *c* acquires a white heat. The progress of the operation can be watched by occasionally removing the stone peg in the trial hole of the furnace cylinder *c*. The heat very slowly ascends into the upper cylinder, and it never becomes so great in the upper as in the lower cylinder. The greatest fusing power of the furnace is confined within a vertical space of about six inches, reckoning from the bottom. The power of flint pebbles to abstract heat from the gases which pass through this apparatus is quite remarkable. When about six inches of pebbles lie above the crucible, and the crucible and the pebbles about it have been white-hot for half an hour, the hand can be held over the top of the furnace, within a few inches of the pebbles, without inconvenience. It becomes wetted with the vapour which rises from the furnace, but feels only a moderate degree of heat.

This form of furnace is attended with the inconvenience that the condition of the matter contained in the crucible cannot be examined, so as to ascertain when the heat has been continued long enough. In cases where the fusion is performed repeatedly on the same weight of metal, this would be of no importance, because the power of the furnace is so steady and regular, that the time of firing which has been found to answer once will answer the same purpose again.

When it is supposed that the fusion of the metal submitted to trial is completed, the



gas is first to be turned off, and then the supply of air stopped. The furnaces may either be allowed to remain intact till it is cold, or it may be lifted off the cylinders *etc* with tongs, and the hot stones allowed to fall into the iron pan placed below the furnace to receive them. A few bricks should be laid between the pan and the table or stool on which it rests, if the latter is made of wood; because the heat given off by the pebbles is very great. The pebbles being raked away from the crucible, the contents of the latter can be examined.

Mr. Griffin has also contrived forms of the gas-furnace provided with a lifting apparatus to afford access to the crucible during the progress of the operation. For figures and descriptions of these, see *Griffin's Chemical Recreations*, 10th edition; also *Griffin's Scientific Circular*, December 1859.

**Gore's Gas Furnace.** This furnace, invented by Mr. G. Gore, of Birmingham (who has kindly communicated the description), is similar in principle to the furnace represented in figure 500, and is well adapted for heating small crucibles to high temperatures.

▲ (Fig. 507) is a cylinder of fire-clay about 9 inches high and 6 inches diameter, open at both ends, and with a hole in its side near the bottom to lead into the chimney; it is covered by a movable plate of fire-clay, *b*, with a hole in its centre for introduction of the crucible or of substances to be melted: this hole is closed by a perforated plug of fire-clay, *c*, for access to the contents of the crucible; and that again is closed by another stopper of clay, *d*. *m* is a chimney of sheet iron about 5 or 6 feet high, kept upright by a ring of iron, *f*, attached to the top of the furnace.

The fireclay cylinder is enclosed in a sheet iron casing with a bottom of iron, to which are fixed three iron legs, *g*. An iron tube, *x*, with a prolongation, *1*, supports, by means of the screw, the burner *κ* and its tube *1*, which is open at both ends. Gas is supplied to the burner by means of the tap *κ*, which has a small index *η*, attached to it for assistance in adjusting the gas.

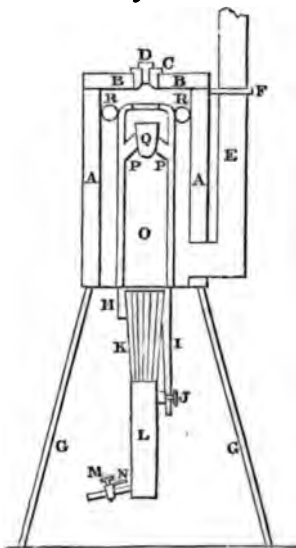
Inside the larger cylinder is another fire-clay cylinder or cupola, o, with open ends, and with three projections of fire-clay, p, for supporting the crucible q; it is kept steady by means of three clay marbles, r.

The gas-burner is a thin metal cylinder deeply corrugated at its upper end, with the corrugations diminishing to nothing at its lower end.

The action of this furnace is as follows:—Gas is admitted to the open tube *L* by the tap *M*; it there mixes with air to form a nearly explosive mixture, which ascends through the burner and burns in the clay cylinder, *o*, being supplied with the remainder of air necessary to complete combustion through the tube *N*, to the outer surface of the flame by means of the spaces between the corrugations. The flame and products of combustion pass up through the cylinder *o*, and then downwards outside it to the chimney, the point of greatest heat being at *q*. It is important in using this furnace that the burner be placed quite in the centre of the bottom of the tube *o*; also that a crucible of not too large nor too small dimensions be selected. The most suitable way of supporting a smaller crucible is by placing it in a larger one that has had its upper parts broken off. If desirable, a little clay luting may be placed round the top edge of the iron casing to exclude air entering between it and the cylinder; also a little thin clay luting upon the part of the bottom of the furnace where the inner cylinder rests.

In lighting the furnace, the plugs c and d are removed, a light held within the opening, and the gas turned on full; should the flame blow down to the bottom of the tube L on lighting (which, however, rarely occurs unless the furnace is already hot), the gas must be turned off and the bottom end of L momentarily closed whilst lighting the gas as before. Should the flame not burn down to the burner, but only burn at the orifice in the clay plate a, it must at once be extinguished and relighted, otherwise some of the gaseous mixture will pass into the chimney unburned, and subsequently ignite and cause an explosion. A large flame now issues from the top orifice, and is white if too much gas is on, and violet or red with the proper quantity. This flame generally diminishes and nearly disappears into the body of the furnace in the course of one minute: whether it does or not, the annular plug c should now be inserted, which

**Fig. 507.**





will compel it to pass downwards to the chimney; and as soon as the small remaining flame disappears or nearly disappears, as it will in a few seconds, the small stopper *d* should also be inserted; instead of this the large flame may be deflected against the chimney by means of a shoot or bent piece of sheet iron until it withdraws inwards; the plugs *c* and *d* may then be reinserted, and the gas-tap partly adjusted. The crucible may be placed in the furnace either before or some time after the act of lighting, but not *immediately* after (if the furnace is cold), or explosions may occur by unburned gaseous mixture passing the crucible into the chimney and igniting afterwards.

After about five minutes, the gas should be adjusted until a sound is heard inside like a series of small explosions. This sound is sometimes not very distinct, especially at high temperatures, and therefore requires a little experience in the use of the furnace in order to be detected; it is, however, a chief guide in determining the proper amount of gas, and should therefore be carefully studied. To assist in adjusting the gas, it will be found very useful to place a small piece of looking-glass beneath the tube *l*, and to adjust the gas-tap until the flame between the burner and the crucible appears wholly violet or slightly white; but this test is liable to fallacy if employed when the gas is just lighted, because the coldness of the parts makes the flame much whiter than it otherwise would be; it is also fallacious when the flame is very hot, the flame appearing whiter than it really is; it is, however, of great assistance at intermediate temperatures. A rough deposit of carbon upon the outer edge of the crucible indicates an excess of gas.

Less gas is required with a crucible in the furnace than without one; also less is necessary when the small hole at the top of the furnace is open than when it is closed; and less is also required when the furnace is cold than after it has been lighted some time, because the draught gradually increases and draws in more air. After having accurately adjusted the gas, no further attention to the furnace is requisite.

Having once found the proper adjustment of gas under certain known circumstances, it is well to notice the position of the index *x*, in order to be able at once to adjust it to the right point on other occasions. The gas should be supplied by a pipe of not less than  $\frac{3}{16}$ ths of an inch bore, with a main pipe of half an inch; but all depends upon the pressure of gas at the particular locality, which is very variable. The consumption of gas varies from 30 to 40 cubic feet per hour.

The top of the chimney should be placed in a position where the products of combustion can pass freely away; if it is placed in an opening or pipe leading to another chimney, care must be taken not to have the draught too powerful, otherwise the heat will be drawn more into the chimney, and the supply of gas in the daytime may be found rather deficient. The furnace will act satisfactorily, though less powerfully, with the chimney standing in an open room, without any special outlet for the products of combustion, provided the full height (6 feet) of chimney is employed; under other circumstances a chimney  $4\frac{1}{2}$  or 5 feet in height may be used.

This furnace will readily melt half a pound of copper, or six ounces of cast iron. It requires from 20 to 30 minutes to acquire its highest temperature; and *then the entrance part of the chimney exhibits a faint red heat in daylight*; if it exhibits much more than this, the draught is too powerful.

When the small hole *d* is open, some air is drawn in that way, and less air passes up with the gas through the tube *o*; but this cold air does not much diminish the temperature of the crucible, because it combines with the excess of gas now passing over the edge of the inner cylinder; it however renders the flame round the crucible white by deficiency of air, and this should be partly corrected by lessening the amount of gas. An excess either of air or gas renders the surface of melted copper dull.

When it is desirable to avoid entirely the contact of air with the fused substance during manipulation, a thin and narrow ring of fireclay should be placed upon the top of the tube *o*, to contract its opening; the flame then completely closes over the top of the crucible and prevents access of air. A proper adjustment of gas, together with exclusion of air in this manner, enables a perfectly bright surface of melted copper, or even tin, to be continuously maintained, from which the images of the parts above are clearly reflected. The clay ring may be withdrawn by lifting the plate *n*. A less perfect exclusion of air may be obtained by employing a narrow crucible placed rather low down in its support. A small iron dish should be placed beneath the tube *l*, to receive any melted substance that may fall.

For descriptions of gas-furnaces for organic analysis, see vol. i. p. 229.

**GASES, ABSORPTION OF, BY LIQUIDS AND SOLIDS.** All solid and liquid substances absorb, or condense in their pores, or on their surfaces, certain definite quantities of every gaseous body with which they are placed in contact. The amount of gas thus absorbed depends, in the first place, on the properties, both chemical and physical, of the bodies brought together, and, secondly, on the temperature and pressure under which the absorption occurs.



As a general rule solids absorb less gas than the same volume of liquid bodies; and in the case of solids, those of which a given weight contains the largest surface or which are most porous take up the largest quantity of gas. We are as yet altogether unacquainted with the law which regulates the amount of gas absorbed by any solid or liquid substance under any condition whatever; any knowledge which we possess concerning the absorptive powers of bodies for gases must therefore be entirely empirical. The volume of a gas which, under certain fixed conditions of temperature and pressure, is absorbed by the unit-volume of any solid or liquid, is a fixed and definite quantity, and is called the "Coefficient of Absorption" of the body for that particular gas. These coefficients of absorption have been determined with accuracy for various liquid and gaseous bodies, and certain relations existing between the volume of gas and the temperature and pressure under which it is absorbed have been satisfactorily established. In the case of solid bodies, on the other hand, the coefficients of absorption are not capable of such easy and accurate determination, partly owing to the impossibility of obtaining the solid matter always under like conditions as regards its state of aggregation, and partly because the amount of gas absorbed by solid bodies is in general extremely small.

1. *Absorption of Gases by Liquids.*—Gases are absorbed by liquids under two distinct sets of laws, according as the gas enters into chemical combination with the liquid or not. Absorptions of the one class are simple chemical combinations, in which the gas is absorbed in fixed proportions, regulated by the known laws of chemical action, independent of alterations of pressure or temperature; examples of this class of phenomena are found in the absorption of carbonic acid or chlorine gas by a solution of caustic soda, or that of chlorine or hydrochloric acid gas by alcohol. The second class of absorptions includes the cases in which the absorbed gas does not enter into any definite chemical combination with the absorbing liquid, and its amount is variable with the temperature and pressure under which the saturation occurs. The one class we may term chemical, the other physical absorptions. Of the phenomena of chemical absorptions we shall not here treat, except in a few cases in which a gas enters into chemical combination with a liquid, by which, at the same time, it is absorbed physically. It is the phenomena of, and the laws relating to, the physical absorption of gases, which here more immediately concern us.

The amount of a gas absorbed by a liquid upon which it exerts no direct chemical action, is dependent: (1.) on the specific nature of the gas and of the liquid; (2.) on the temperature at which the absorption takes place; (3.) on the pressure under which the absorption takes place. That the amount of absorbed gas depends in the first place upon the chemical nature of the gas and of the liquid, is seen from the fact that the solubility of different gases in the same liquid and of the same gas in different liquids, varies extremely. Thus, for example, 1 volume of water at  $0^{\circ}\text{C}$ . absorbs 0.00193 volumes of hydrogen, 1.7967 volumes of carbonic acid, and 1180.0 volumes of ammonia; thus, too, whilst 1 volume of water at  $0^{\circ}\text{C}$ . absorbs only 0.2563 volumes of olefiant gas, 1 volume of alcohol at the same temperature, absorbs 3.595 volumes.

The law which expresses the relation existing between the quantity of any absorbed gas and the temperature, appears to be an extremely complicated one, to the nearer acquaintance with which we have at present but little clue; so that the variation of the amount of absorbed gas with the temperature must in every case be determined by direct experiment. As a general rule, the volume of gas absorbed decreases with increase of temperature, and *vice versa*; thus 1 volume of water at  $0^{\circ}\text{C}$ . dissolves 68.61 volumes of sulphurous acid, but the same volume of water at  $24^{\circ}$  dissolves only 31.8 volumes; thus also, 1 volume of alcohol at  $0^{\circ}$  absorbs 17.891 volumes of sulphuretted hydrogen gas, whereas at  $24^{\circ}$  the quantity absorbed is only 5.955 volumes. This rule is, however, not without its exceptions; thus, for example, hydrogen is equally soluble in water between the temperatures of  $0^{\circ}$  and  $25^{\circ}$ , 1 volume of water between these temperatures dissolving 0.0193 volume of this gas; and thus also, for temperatures varying from  $0^{\circ}$  to  $20^{\circ}$ , 1 volume of alcohol dissolves a constant amount of oxygen, namely, 0.284 volume. In the case of many of the less soluble gases, the alteration in the absorbed volume effected by changes of temperature lying within the range of easy experimentation is so small, that it can only be detected by accurate observation; indeed, the earlier chemists, especially Dalton, believed that the amount of gas absorbed was entirely independent of the temperature.

A simple relation has, however, been found to exist between the amount of absorbed gas and the pressure under which the absorption takes place. Within certain limits, which we shall presently more nearly define, the quantity or weight of gas absorbed varies directly as the pressure. The general fact that under increased pressure the amount of absorbed gas is greater, has been known for a long time, and was pointed out by Cavendish and Priestley; but the exact law was first enunciated by William



Henry, in the *Philosophical Transactions* for 1803, in the following words:—"Under equal circumstances of temperature, water takes up, in all cases, the same volume of condensed gas as of gas under ordinary pressure. But as the spaces occupied by every gas are inversely as the compressing force, it follows that water takes up of gas condensed by one, two, or more additional atmospheres, a quantity which, ordinarily compressed, would be equal to twice, thrice, &c. the volume absorbed under the common pressure of the atmosphere." Thus, for instance, water at 15° C. absorbs its own bulk of carbonic acid under whatever pressure the absorption may take place; and if the pressure in the one case be 1, and in the other 2, 3, 4, &c., the quantity or weight of gas absorbed under the various pressures is as 1 to 2, 3, 4, &c.

This simple relation holds good within certain limits only, because Boyle's law (that the volume of a gas is inversely proportional to the pressure to which it is subjected), upon which this relation is based, is strictly correct for all gases only within a certain range of pressure, and in the case of the more condensable gases, as carbonic acid and ammonia, this range does not diverge far beyond the ordinary pressure of the atmosphere. The exact limit above and below the normal atmospheric pressure at which this relation of the absorbed quantity of gas to the pressure ceases to be exact, has as yet been experimentally determined in one or two cases only.

When a mixture of two or more gases is allowed to remain in contact with a liquid with which none of the gases enter into chemical combination, a portion of each gas is absorbed; but the liquid does not dissolve so much of any one gas as it would have done if that gas alone had been present. The quantity of each gas absorbed, is in this case also dependent upon the pressure which each gas exerts on the liquid. When two or more gases having the volumes  $v$ ,  $v_1$ ,  $v_2$ , &c. each measured under the pressure  $P$ , are brought together, they diffuse into each other until the particles of each are extended equally throughout the total space. If the pressure which the gas  $v$  exerts before mixing was  $P$ , the pressure after mixing,  $P_1$ , is, according to Boyle's law, equal

to  $\frac{v}{v + v_1 + v_2} \cdot P$ ; that on  $v_1$  is  $\frac{v_1}{v + v_1 + v_2} \cdot P$ ; and that on  $v_2$  is  $\frac{v_2}{v + v_1 + v_2} \cdot P$ ,

the sum of these pressures being equal to the original pressure  $P$ . This pressure exerted by one of a mixture of gases on the inclosing space may be termed "partial pressure," in contradistinction to the sum of these or the "total pressure." As the amount of a single gas absorbed by a liquid is proportional to the total pressure of the experiment, so, in a mixture of gases, is the absorbed amount of each proportional to the partial pressure on that gas. This law regulating the absorption of mixed gases by liquids (which, in fact, includes Henry's law for total pressures), was first stated by Dalton in a paper on the absorption of gases in liquids, published in the *Manchester Memoirs* for 1805, containing a masterly theoretical treatment of the whole subject. In this paper, Dalton discusses all the cases of the absorption of gases by liquids, and develops the law which regulates the absorption of two or more gases when their volume is infinitely large as compared with that of the absorbing liquid, as also the law regulating the absorption when the volume of the gases has a finite relation to the liquid, showing in this last case, that the absorptometric equilibrium occurs when the pressure of each gas dissolved in the liquid is equal to that of the portion of the gas which remains unabsorbed above the liquid. Although, as we shall see, these theoretical results are correct, still many of Dalton's ideas regarding absorption, being founded on incomplete and inaccurate data, have since proved false; thus for instance, he pictured to himself the act of absorption as nothing else than an infiltration of the liquid by the molecules of the gas, and hence assumed, his experiments not teaching him otherwise, that all non-viscous liquids absorb a like quantity of the same gas, and that temperature does not affect the absorption; and he expresses the difficulty which he has to account for the fact, too evident to be overlooked, that different gases are absorbed by the same liquid in such very various quantities.

Hence, owing to the incomplete nature of Dalton's experiments, and notwithstanding the fact that Saussure afterwards occupied himself with the subject, the law of pressures must be considered as having remained without a sound experimental basis, until the recent exact determinations of Bunsen and his pupils \* placed the question beyond a doubt, proving that, within the limits before mentioned, the laws of Dalton and Henry are founded on fact.

In order to be able to compare the solubility of the various gases in liquids, it is usual to determine the volume of gas, measured at the standard temperature and pressure (0° C. and 0.76m. pressure of mercury), which is absorbed under a pressure of 0.76m. of mercury in 1 volume of liquid at the temperature of observation, and this volume is called the "Coefficient of Absorption" of the gas in the liquid.

\* See Bunsen's *Gasometric Analysis*, London: Walton and Maberly, 1857, article, Absorption; also *Phil. Mag.* [4] ix, 116 and 181; also *Ann. Ch. Pharm.* xciv. 129; xcv. 1; xcix. 129; also *Chem. Soc. Qu. J. vol. 18.*



The methods adopted by Bunsen and his pupils for the determination of the coefficients of absorption of gases by water and alcohol,—for these are the only liquids which have as yet been employed,—varied according to the solubility of the gas in the liquid used. In the case of the very soluble gases, the amount of the absorbed gas was determined chemically; in the case of the less soluble gases, a peculiar eudiometric process was adopted.

The gases whose solubility has been determined by chemical methods are, *sulphuretted hydrogen, sulphurous acid, ammonia, and chlorine*; these gases, evolved in a state of purity, were passed for a long time through a large volume of liquid, which had been freed from air by long continued boiling, and was kept at a constant temperature during the experiment. After the gas had passed so long through the liquid that the latter was completely saturated, the barometric pressure was read off and a known volume of the liquid was withdrawn, special precautions to avoid possible loss of gas being observed, and the gas contained in this liquid quantitatively determined either by means of volumetric analysis or by the other ordinary processes of analytical chemistry.

If the volume of the liquid does not undergo any appreciable increase in bulk, owing to the absorption of the gas, we are able easily to calculate the coefficients of absorption from the data obtained by this process. If, however, as is the case with all the more soluble gases, the volume of the saturated liquid is considerably larger than that of the liquid before saturation, it is necessary, either to determine the amount of this increase of bulk, or, what is the same thing, the specific gravity of the saturated solution, or else, by a modification of the process, to saturate only a small volume of liquid, and to determine the absolute quantity of gas absorbed, by weighing before and after the saturation. As an example of this calculation, we may choose an actual experiment of the determination of the solubility of sulphurous acid in absolute alcohol at  $20^{\circ}$ . It was found that 4 volumes of the alcohol saturated with sulphurous acid at  $20^{\circ}$  C. and under a pressure of 3.7438 m. of mercury, contained 1.092 grms. of sulphurous acid:—required the volume of gas at  $0^{\circ}$  and 0.76 contained in the unit-volume of pure alcohol, when the specific gravity of the saturated solution at  $20^{\circ}$  is 0.9404, and that of the pure alcohol 0.792? From these data we find that the weight of the measured volume is 3.7616 grms.; and 2.6696 grms. is the weight, or 3.371 c.c. the volume of alcohol which absorbed 1.092 grms. of sulphurous acid at  $20^{\circ}$ , and under the pressure of 0.7438 m.; so that, according to Henry's law, the quantity which would have been absorbed under a pressure of 0.760 m. is 1.115 grms.; and as one cubic centimetre of sulphurous acid gas at  $0^{\circ}$  and 0.76 weighs 0.002861 grms., the volume of gas at  $0^{\circ}$  and 0.76 absorbed by 3.371 c.c. alcohol is 389.8 c.c.; or the coefficient of absorption of sulphurous acid in alcohol at  $20^{\circ}$  is 115.7.

For the determination of the coefficients of absorption of gases less soluble in the liquid employed, Bunsen has constructed an instrument termed an "Absorptiometer," represented in *figs. 508 and 509*, which he thus describes:—"The absorption tube *e*, *fig. 508*, divided into millimetres and calibrated, has a small iron band *b*, *fig. 509*, furnished with a screw luted on to its lower and open end; this fits into another screw attached to the small iron stand *a a*. By means of this arrangement, the open end of the tube can be screwed down against a plate of caoutchouc covering the bottom of the stand, and the tube thus completely closed. On each side of the stand are fixed two steel springs, *c c*, which fit into two vertical grooves inside the wooden foot of the apparatus *f*, *fig. 508*, so that the little iron stand *a a*, *fig. 509*, can be raised or depressed, but not turned on its axis horizontally. The outer cylinder, *g g*, *fig. 508*, is not cemented into the wooden foot *f*, or into the iron rim *h*, but the ground glass edges of the cylinder are pressed against caoutchouc rings, inserted in the foot and in the rim by means of the screws *i i*. The tubes *rr* serve to

Fig. 508.



Fig. 509.



raising or depressing the level of the mercury in the inner glass cylinder. The temperature of the surrounding water is determined by the small thermometer *k*. The upper end of the outer cylinder is closed by an iron lid having a hinge at one side, and fastened down by means of a nut and screw attached to the iron rim *h*, fitting into a groove *p*, in the side of the lid. In the inside of the lid there is a raised rim of iron, over which a thick sheet of caoutchouc is extended and fastened by a screwed ring *s*. This distended caoutchouc serves as a spring against which the top of the tube can be pressed, keeping it in a fixed position during the violent agitation necessary for the process of absorption.

The mode of using this apparatus, and the method of calculation employed in these experiments, is best explained by an actual example. We select for this purpose the determination of the coefficient of absorption of nitrogen in water at  $19^{\circ}\text{C}$ . A certain quantity of the gas under examination is placed in the absorption tube, over mercury in the mercurial trough, and its volume determined, the usual precautions as to reading off pressure, temperature, &c. being taken, as in the ordinary process of gas analysis. The following observations are made:

Lower surface of mercury in outer cylinder	. . . . .	$a = 423.6$ mm.
Upper surface of mercury in absorption tube	. . . . .	$b = 124.1$ "
Barometric pressure	. . . . .	$p = 746.9$ "
Temperature of the absorptiometer	. . . . .	$t = 19.2^{\circ}\text{C}$ .
Temperature of the barometer	. . . . .	$\tau = 19.0^{\circ}$ "

A quantity of water perfectly freed from air is next introduced under mercury into the tube, which is then screwed tightly against the caoutchouc plate, and the tube thus closed, is placed in the cylinder *g g*, containing some mercury, and over that a quantity of water. As soon as the pressure within and without has been equalised by slightly turning the tube, it is again closed, and the whole apparatus rapidly agitated for about a minute. This agitation, with opening and closing of the tube, is continued many times, until no further change of volume is perceptible. The observations necessary for the measurement and reduction of the residual gas are thus made:

Level of mercury in outer cylinder	. . . . .	$a' = 352.2$ mm.
Level of mercury in absorption tube	. . . . .	$b' = 350.7$ "
Upper level of water in absorption tube	. . . . .	$c' = 65.6$ "
Upper level of water in outer cylinder	. . . . .	$d' = 8.0$ "
Barometric pressure	. . . . .	$p' = 746.3$ "
Temperature of the absorptiometer	. . . . .	$t' = 19.0^{\circ}\text{C}$ .
Temperature of the barometer	. . . . .	$\tau' = 18.9^{\circ}$ "

From the first series of observations, the pressure on the dry nitrogen is obtained by subtracting the height of the column of mercury in the tube, ( $a - b = 299.5$  mm.), and the tension of the vapour of water at  $19.2^{\circ}$  ( $= 16.6$  mm.), from the barometric pressure, the height of both the columns of mercury being corrected for the expansion which they undergo in being heated from  $0^{\circ}$  to  $19.2^{\circ}$ . This pressure,  $P$ , is found to be equal to  $744.4 - 298.5 - 16.6 = 429.3$  mm.

The volume of nitrogen employed, when reduced to  $0^{\circ}$ , is, according to the table of capacity of the instrument, found to be  $32.608 = V$ , expressed in arbitrary units. The barometric pressure, corrected for expansion, after the experiment, is  $743.8$  mm.; the height of the corrected column of mercury inside the tube, is  $1.5$  mm.; the height of the column of water in the tube is  $285.2$  mm.; that in the outer cylinder  $344.2$  mm.; so that the column of water which has to be added to the barometric pressure is  $344.2 - 285.2 = 59.0$  mm., equal to  $4.4$  mm. of mercury; the tension of the vapour of water at  $19.2^{\circ}$  is  $16.3$  mm.; and hence the pressure on the unabsorbed nitrogen is  $P_1 = 743.8 + 4.4 - 1.5 - 16.3 = 730.5$  mm.

The volume of unabsorbed gas, reduced to  $0^{\circ}$ , is found from the table of capacity to be  $16.522 = V_1$  of the same arbitrary units, whilst the volume of water employed is  $182.37 = h$  units.

From these data, the coefficient of absorption can be easily obtained. The volume of nitrogen reduced to the pressure  $760$  mm. was, before the absorption,  $\frac{VP}{760}$ ; the re-

duced volume after the absorption is  $\frac{V_1P_1}{760}$ ; and hence the volume absorbed under the pressure  $P_1$  is  $\frac{VP}{760} - \frac{V_1P_1}{760}$ . If now the law of Henry be correct in the case of nitrogen and water, the volume of gas absorbed under the pressure of  $760$  mm. will be greater than that absorbed under the pressure  $P_1$  in the proportion  $\frac{760}{P_1}$ ; or it will be

$\frac{VP}{P_1} - V_1$ . Hence the volume of gas absorbed by the unit-volume of liquid in the co-efficient of absorption is:

$$C = \frac{1}{K} \cdot \left( \frac{VP}{P_1} - V_1 \right),$$

or, for the special case we are considering:

$$C = \frac{1}{182.37} \cdot \left( \frac{32.608 \times 429.3}{730.5} - 16.522 \right) = 0.01448.$$

It is absolutely essential that the liquids employed in these absorptiometric determinations be freed completely from air or other gases held in solution; this is best accomplished by continuous boiling in a flask whose neck has been drawn out to a fine point before the blowpipe, so that the flask can be instantly hermetically sealed. The vessel containing the liquid, which ought to strike against the glass like a water-hammer, is opened under mercury, and thus all possible entrance of air is prevented.

By the help of this instrument, and by the application of a method of calculation similar to the example just cited, the following coefficients of absorption in water and absolute alcohol were experimentally determined. In cases in which the solubility of the gas varied with the temperature, a simple interpolation formula,  $c = A + Bt + Ct^2$ , serves to express the relation with sufficient exactness.

1. *Nitrogen*.—The nitrogen was prepared by passing atmospheric air, freed from carbonic acid and ammonia, over red-hot copper turnings.

In water (from 0° to 20° C.);  $c = 0.020346 - 0.00053887t + 0.000011156t^2$ .

In alcohol\* (from 0° to 25° C.);  $c = 0.126338 - 0.000418t + 0.000006t^2$ .

From these formulae the following coefficients are calculated:

For Water.				For Alcohol.			
0° C.	0.02035	12° C.	0.01549	0° C.	0.12634	14° C.	0.12166
2°	0.01932	14°	0.01500	2°	0.12553	16°	0.12119
4°	0.01838	16°	0.01458	4°	0.12476	18°	0.12076
6°	0.01752	18°	0.01426	6°	0.12404	20°	0.12038
8°	0.01657	20°	0.01403	8°	0.12338	22°	0.12005
10°	0.01607			10°	0.12276	24°	0.11976
				12°	0.12219		

2. *Hydrogen*.—The hydrogen was prepared from pure zinc and sulphuric acid.

In water (from 0° to 20° C.);  $c = 0.0193$ .

In alcohol (from 0° to 25° C.);  $c = 0.06925 - 0.0001487t + 0.000001t^2$ .

Hence:

In Water.		In Alcohol.			
$c = 0.0193$		0° C.	0.02569	10° C.	0.06786
constant.		2°	0.06896	12°	0.06761
		4°	0.06867	14°	0.06731
		6°	0.06839	16°	0.06713
		8°	0.06813	18°	0.06690
				20° C.	0.06668
				22°	0.06646
				24°	0.06626

3. *Carbonic Oxide*.—Prepared by heating pure formate of magnesia with strong sulphuric acid; treatment with a potash-ball showed that the gas was pure.

In water (from 0° to 20° C.);  $c = 0.032874 - 0.00081632t + 0.000016421t^2$ .

In alcohol (from 0° to 25° C.);  $c = 0.20443$ .

Hence:

For Water.				For Alcohol.	
0° C.	0.03287	8° C.	0.02739	16° C.	0.02402
2°	0.03131	10°	0.02635	18°	0.02350
4°	0.02987	12°	0.02544	20°	0.02312
6°	0.02857	14°	0.02466		
				$c = 0.20443$	
				constant.	

4. *Carbonic Acid*.—Prepared by the action of strong sulphuric acid on chalk, due precautions as to its purification being taken.

In water (from 0° to 20° C.);  $c = 1.7967 - 0.07761t + 0.0016424t^2$ .

In alcohol (from 0° to 25° C.);  $c = 4.32955 - 0.09395t + 0.00124t^2$ .

\* The coefficients of absorption for all the following gases in alcohol were determined by Carlius. See Ann. Ch. Pharm. xcix. 129.



Hence:

<i>For Water.</i>				<i>For Alcohol.</i>			
0° C.	1.7967	12° C.	1.1018	0° C.	4.3295	14° C.	3.2573
2°	1.6481	14°	1.0321	2°	4.1466	16°	3.1438
4°	1.5126	16°	0.9753	4°	3.9736	18°	3.0402
6°	1.3901	18°	0.9318	6°	3.8105	20°	2.9465
8°	1.2809	20°	0.9014	8°	3.6573	22°	0.28628
10°	1.1847			10°	3.5140	24°	2.7890
				12°	3.3807		

5. *Marsh Gas*.—The gas employed for the experiments with water was collected from the mud-volcanoes at Bulganak in the Crimea, and being preserved in sealed tubes was shown by analysis to contain neither oxygen, nitrogen, carbonic acid, nor olefiant gas. The gas used for the alcohol-absorption was prepared by the usual process from acetate and hydrate of potassium, and eudiometric analysis showed that it was pure.

In water (from 0° to 20° C.);  $c = 0.05449 - 0.0011807 t + 0.000010278 t^2$ .

In alcohol (from 0° to 24° C.);  $c = 0.522586 - 0.0028655 t + 0.0000142 t^2$ .

Hence:

<i>For Water.</i>				<i>For Alcohol.</i>			
0° C.	0.05449	12° C.	0.04180	0° C.	0.52259	14° C.	0.48525
2°	0.05217	14°	0.03997	2°	0.51691	16°	0.48037
4°	0.04993	16°	0.03823	4°	0.51185	18°	0.47561
6°	3.04778	18°	0.03657	6°	0.50590	20°	0.47096
8°	0.04571	20°	0.03499	8°	0.50057	22°	0.46642
10°	0.04372			10°	0.49535	24°	0.46199
				12°	0.49024		

6. *Ethylene*.—Prepared in the usual manner from alcohol and sulphuric acid; all traces of alcohol and ether-vapour and of higher hydrocarbons, were removed by absorbing a large portion of the collected gas by strong sulphuric acid before the experiment. Eudiometric analysis proved the purity of the gas.

In water (from 0° to 20° C.);  $c = 0.25629 - 0.00913631 t + 0.000188108 t^2$ .

In alcohol (from 0° to 24° C.);  $c = 3.59498 - 0.057716 t + 0.0006812 t^2$ .

Hence:

<i>For Water.</i>				<i>For Alcohol.</i>			
0° C.	0.2563	12° C.	0.1737	0° C.	3.5950	14° C.	2.9205
2°	0.2388	14°	0.1652	2°	3.4823	16°	2.8459
4°	0.2227	16°	0.1583	4°	3.3750	18°	2.7768
6°	0.2082	18°	0.1528	6°	3.2732	20°	2.7131
8°	0.1952	20°	0.1488	8°	3.1768	22°	2.6549
10°	0.1837			10°	3.0859	24°	2.6022
				12°	3.0006		

7. *Nitrous Oxide*.—The gas was prepared from pure nitrate of ammonium.

In water (from 0° to 24° C.);  $c = 1.30521 - 0.045362 t + 0.0006843 t^2$ .

In alcohol (from 0° to 24° C.);  $c = 4.17805 - 0.69816 t + 0.000609 t^2$ .

Hence:

<i>For Water.</i>				<i>For Alcohol.</i>			
0° C.	1.3052	14° C.	0.8034	0° C.	4.1780	14° C.	3.3200
2°	1.2172	16°	0.7535	2°	4.0409	16°	3.2169
4°	1.1346	18°	0.7090	4°	3.9086	18°	3.1187
6°	1.0575	20°	0.6700	6°	3.7811	20°	3.0253
8°	0.9858	22°	0.6364	8°	3.6585	22°	2.9368
10°	0.9196	24°	0.6082	10°	3.5408	24°	2.8532
12°	0.8588			12°	3.4279		

8. *Nitric Oxide in Alcohol*.—The pure gas was prepared by passing the mixture of gases evolved by the action of nitric acid on copper, into a concentrated solution of protosulphate of iron. The pure gas was collected by gently warming this saturated solution.

In alcohol (from 0° to 24° C.);  $c = 0.31606 - 0.003487 t + 0.000049 t^2$ .

Hence:

<i>For Alcohol.</i>			
0° C.	0.3661	8° C.	0.2913
2°	0.3093	10°	0.2861
4°	0.3029	12°	0.2813
6°	0.2969		
		14° C.	0.2768
		16°	0.2728
		18°	0.2692
		20° C.	0.2659
		22°	0.2631
		24°	0.2605

9. *Ethyl-gas in Water*.—The gas used in these experiments was prepared by the action of zinc-ethyl upon iodide of ethyl.

In water (from 0° to 20° C.);  $c = 0.031474 - 0.0010449 t + 0.000025066 t^2$ .

Hence:

*For Water.*

0° C.	0.03147	6° C.	0.02613	12° C.	0.02257	18° C.	0.02084
2°	0.02947	8°	0.02474	14°	0.02179	20°	0.02064
4°	0.02770	10°	0.02355	16°	0.02121		

10. *Methyl-gas in Water*.—Prepared by the action of zinc-methyl upon iodide of methyl.

In water (from 0° to 20° C.);  $c = 0.0871 - 0.0033242 t + 0.0000603 t^2$ .

Hence:

*For Water.*

0° C.	0.0871	6° C.	0.0693	12° C.	0.0559	18° C.	0.0468
2°	0.0807	8°	0.0644	14°	0.0524	20°	0.0447
4°	0.0748	10°	0.0599	16°	0.0492		

11. *Oxygen in Water*.—The coefficients of absorption of oxygen in water were not determined directly by the process described, because it was found that although the mercury contained in the absorption tube was purified as completely as possible, it still contained traces of foreign metals, which on agitation were oxidised at the expense of the dissolved gas, thus rendering the determination of the coefficients of absorption incorrect.

In order to determine the solubility of oxygen in water, the following indirect method was adopted, which, however, presupposes the applicability of Dalton's law of partial pressures. If both oxygen and nitrogen obey this law, it is not difficult from the known coefficients of absorption of nitrogen, from the known composition of the air, and from the relative amounts of the two gases dissolved when water is saturated with air, to calculate the coefficients of absorption of oxygen in water. The relative quantities of oxygen and nitrogen dissolved in water through which air was passed to saturation were found by experiment to remain constant; that is, at all the observed temperatures, the quantity of oxygen contained in 100 parts of absorbed gas is 35.91 =  $V^o$ , and that of nitrogen 65.09 =  $V^a$ . Hence we see that, as the total amount of air absorbed at different temperatures varies, the curve representing the relation between the amount of absorbed oxygen and the temperature, must be parallel with the curve representing the same relation for nitrogen.

The composition of one volume of the atmosphere we may take to be 0.2096 =  $O$  volume of oxygen, and 0.7904 =  $N$  volume of nitrogen; if now,  $C^o$  represent the coefficient of absorption of oxygen, and  $C^a$  that of nitrogen at any given temperature, the volumes of absorbed oxygen and nitrogen contained in the volume  $V$  of air absorbed under the pressure  $P$ , are, according to Dalton's law,—

$$V^o = \frac{C^o V O P}{0.76 (N + O)}; \text{ and } V^a = \frac{C^a V N P}{0.76 (N + O)};$$

hence by division we have

$$C^o = C^a \frac{V^o N}{V^a O}; \text{ or } C^o = C^a \frac{35.91 \times 0.7904}{65.09 \times 0.2096} = C^a \times 2.0225$$

or expressed in terms of the temperature alone:

$$(\text{from } 0^\circ \text{ to } 20^\circ); c = 0.4115 - 0.00108986 t + 0.000022563 t^2.$$

And hence:

0°	0.04114.	2°	0.03907.	4°	0.03717.	6°	0.03544.	8°	0.03389.	10°	0.03250.
12°	0.03133.	14°	0.03034.	16°	0.02949.	18°	0.02884.	20°	0.02838.		

12. *Oxygen in Alcohol*.—The determinations of the solubility of oxygen in alcohol were made in the usual way with the absorptiometer, the error arising from oxidation of the metals contained in the mercury proving in this case inappreciable. The quantity of oxygen dissolved in alcohol between 0° and 24° C. remained constant:

$$(\text{from } 0^\circ \text{ to } 24^\circ); c = 0.28397 \text{ constant.}$$

13. *Atmospheric Air in Water*.—When the volume of a mixture of two or more gases is infinitely large as compared with that of the absorbing liquid, the total quantity of gas absorbed, or the coefficient of absorption of the mixture, is easily found from the several coefficients of absorption of the component gases and their relative proportion in the mixture. When the volume of the gas bears a finite relation to that of the absorbing liquid, and the gases are unequally soluble, the alteration effected in the

composition of the gas by the absorption must be brought into consideration. In the following calculations of the solubility of atmospheric air in water, the volume of the gas is considered as infinite compared with that of the water. Hence, as 1 volume of air contains 0.2096 vol. of oxygen, and 0.7904 vol. of nitrogen, the coefficient of absorption of air in water, according to Dalton's law, is  $C^a = C^o \times 0.2096 + C^n \times 0.7904$  where  $C^o$  and  $C^n$  represent the coefficient of absorption of oxygen and nitrogen at the given temperature. The coefficient expressed in terms of the temperature alone is:

$$(\text{from } 0^\circ \text{ to } 20^\circ); c = 0.24706t - 0.000654358t + 0.0000135469t^2.$$

and hence:

0° C. 0.02471	6° 0.02128	12° 0.01882	18° 0.01732
2° 0.02345	8° 0.02034	14° 0.01822	20° 0.01704
4° 0.03227	10° 0.01963	16° 0.01771	

The coefficients of absorption of the following gases, which are much more soluble than the preceding, were determined by the chemical method referred to above. The determinations of the solubility of sulphurous acid, sulphuretted hydrogen, and chlorine in water, were made by Schönfeld (Ann. Ch. Pharm. xcv. 1); those in alcohol by Carius (*loc. cit.*)

14. *Sulphurous Acid in Water*.—The amount of absorbed gas was estimated chemically, by the iodometric method of analysis, reduction being made in the calculation for the alteration of the bulk of the liquid by the absorption of gas.

The following expressions give coefficients which approximate very closely to the observed amounts:

$$(\text{from } 0^\circ \text{ to } 20^\circ) \text{ for pure water; } c = 79.787 - 2.6077t + 0.029349t^2.$$

$$(\text{from } 20^\circ \text{ to } 40^\circ) \text{ " " } c = 76.182 - 2.1716t + 0.01903t^2.$$

Hence the following values:

$$0^\circ 79.789; 10^\circ 56.647; 20^\circ 39.374; 30^\circ 27.161; 40^\circ 18.766.$$

15. *Sulphurous Acid in Alcohol*.—In pure alcohol the coefficient is found from the formula—

$$(\text{from } 0^\circ \text{ to } 24^\circ), c = 328.62 - 16.95t + 0.3119t^2,$$

hence the coefficients are:

$$0^\circ 328.62; 5^\circ 261.67; 10^\circ 190.31; 15^\circ 144.55; 20^\circ 114.48; 24^\circ 101.47$$

16. *Sulphydic Acid in Water*.—The sulphur of the dissolved gas was weighed as sulphate of barium. The interpolation formula obtained from the experiments is—

$$(\text{from } 0^\circ \text{ to } 40^\circ); c = 4.3706 - 0.083687t + 0.0005213t^2,$$

hence the coefficients are

$$0^\circ 4.3706; 10^\circ 3.5858; 20^\circ 2.9053; 30^\circ 2.3290; 40^\circ 1.8569.$$

17. *Sulphydic Acid in Alcohol*.—Experiment gave—

$$c = 17.891 - 0.65598t + 0.00661t^2.$$

Hence:

$$(\text{from } 0^\circ \text{ to } 25^\circ) 0^\circ 17.891; 4^\circ 15.373; 8^\circ 13.066; 12^\circ 10.971; 16^\circ 9.088; \\ 20^\circ 7.415; 24^\circ 5.955.$$

18. *Chlorine in Water*.—The coefficients of chlorine in water cannot be determined below  $10^\circ$ , as at that temperature a crystalline hydrate of chlorine is formed. The quantity of absorbed gas was determined by the iodometric method. Experiment gave the following interpolation formula:

$$(\text{from } 10^\circ \text{ to } 40^\circ) c = 3.0361 - 0.046196t + 0.0001107t^2.$$

Hence:

$$10^\circ 2.5852; 20^\circ 2.2405; 30^\circ 1.7499; 40^\circ 1.3655.$$

18. *Ammonia in Water*.—The solubility of ammonia in water has been determined by Dr. Carius (Ann. Ch. Pharm. xcix. p. 129). The following formula gives the result of his experiments:

$$(\text{from } 0^\circ \text{ to } 25^\circ), c = 1049.63 - 29.496t + 0.067687t^2 - 0.0095621t^3.$$

More recently the solubility of ammonia in water at different temperatures and under direct variation of pressure, has been exactly estimated by Messrs. Roscoe and Dittmar (Chem. Soc. Qu. J. xii. 147). These chemists have shown that the numbers given by Carius are all 10 per cent. too low, owing to the existence of unobserved experimental errors running through his determinations. They have also proved that the quantity of ammonia absorbed by water at a constant temperature is not (as supposed by Carius) proportional to the pressure under which the absorption occurs. This is



clearly seen from the following table, in which (G) gives the weight in grammes of ammonia absorbed by 1 gramme of water at 0° C. under variation of direct pressure (P) from 0.01 m. to 2.0 m. of mercury.

P.	G.	P.	G.	P.	G.	P.	G.	P.	G.
0.01	0.044	0.30	0.515	0.80	0.906	1.30	1.310	1.80	1.906
0.04	0.149	0.40	0.607	0.90	0.968	1.40	1.415	1.90	2.046
0.10	0.275	0.50	0.690	1.00	1.037	1.50	1.526	2.00	2.195
0.15	0.351	0.60	0.768	1.10	1.117	1.60	1.645		
0.20	0.411	0.70	0.840	1.20	1.208	1.70	1.770		

The following numbers give the weight of ammonia absorbed by one gramme of water at the temperatures annexed under the barometric pressure 0.76 m. as found by Roscoe and Dittmar.

	gm.		gm.		gm.		gm.
0° C.	0.875	16°	0.582	32°	0.382	48°	0.244
4°	0.792	20°	0.526	36°	0.343	52°	0.214
8°	0.713	24°	0.474	40°	0.307	56°	0.186
12°	0.645	28°	0.426	44°	0.275		

The experiments which have been made to verify the law of pressures, have been applied not so much to the determination of the exactitude of the law under high pressures, as to the exemplification of the truth of the law of partial pressures. Thus the solubility of carbonic acid, under varying pressures, has only been examined by Bunsen between the limits of 523 and 725 millimetres of mercury, whilst Henry employed a pressure as high as 1.4 metres of mercury. In the case of gaseous mixtures, for which the instrument was more suited, the precision of the law has been demonstrated by a large number of experiments with different gases. Thus, in mixtures of carbonic acid and hydrogen in water, of carbonic acid and carbonic oxide, of carbonic oxide and marsh gas, of carbonic acid and hydrogen, and of carbonic oxide, marsh gas, and hydrogen in alcohol, it has been shown that the component gases are absorbed in quantities exactly regulated by Dalton's law.

In order to understand the mode in which these verifications of the law are obtained, it will be necessary in the first place to develop the general expression for the alterations which a mixture of two gases undergoes on absorption, and then to apply this general formula to special examples. If Dalton's law be correct, that in a gaseous mixture undergoing absorption, when the volume of the liquid is not inappreciable compared with that of the gas, the component gases are dissolved in quantities dependent upon the pressures of the respective components of the residual gas, it will not be difficult to calculate from absorptiometric data the relative proportion of the gases in the unabsorbed residue. If this calculated result agrees with a direct eudiometric analysis, the law is proved to be true. What we have first to calculate is, then, the composition of the residual gas from the other absorptiometric data. For this purpose let all the volumes of gas be reduced to 0° C.; then let the total volume of  $V$  gas employed in the experiment, be under the pressure  $P$ . In the unit-volume of this mixed gas let there be  $v$  volumes of the one, and  $v_1$  volumes of the other gas. Let the coefficient of absorption of the first gas be  $\alpha$ , that of the second  $\beta$ , and the volume of the absorbing liquid  $h$ . Further, let the total volume of the gas remaining after the absorption be  $V_1$ ; and, lastly, let the unit-volume of this gas contain  $u$  volumes of the one, and  $u_1$  volumes of the other constituent gas. These values of  $u$  and  $u_1$  are the unknown quantities which have to be found from the given data.

The volume  $V$  contains  $vV$  volumes of the first gas at the pressure  $P$ , or  $\frac{vVP}{0.76}$  volumes at 0.76. This volume is divided by absorption into two parts; the first part  $x$  remains behind after the absorption as free gas; the second,  $x_1$ , is that absorbed by the liquid. The quantity of this latter is determined by the law of absorption; the unit of liquid absorbs  $\alpha$  volume under the pressure 0.76: hence, under the pressure  $P_1$ ,  $h$  volumes of liquid will absorb  $\frac{\alpha h P_1}{0.76}$ . As, however, the first gas is expanded by mixing with the second, from  $x$  to  $\frac{V_1 P_1}{0.76}$ , the quantity of gas absorbed by  $h$  is, by virtue of the partial pressure  $\frac{\alpha h x}{V_1} = x_1$ . Hence,  $x + \frac{\alpha h x}{V_1} = \frac{vVP}{0.76}$ , and  $x = \frac{vVP}{0.76 \left(1 + \frac{\alpha h}{V_1}\right)}$ ; and, by similar reasoning, the volume of the second residual gas,  $y = \frac{v_1 VP}{0.76 \left(1 + \frac{\beta h}{V_1}\right)}$ .

Hence if  $vVP = A$ ;  $v_1VP = A_1$ ;  $\left(1 + \frac{\alpha h}{V_1}\right) = B$ , and  $\left(1 + \frac{\beta h}{V_1}\right) = B_1$ , we obtain

$$\frac{AB_1}{AB_1 + A_1B} = \frac{x}{x+y} = u \quad (1)$$

$$\frac{A_1B}{AB_1 + A_1B} = \frac{y}{x+y} = u_1$$

The reverse of this calculation is to obtain the composition of the original gaseous mixture from the observed quantities  $V, P, V_1, P_1, \alpha, \beta$ , and  $h$ . In this way an analysis is in fact made of the mixture of gases, without resort to any chemical decomposition; and this absorptiometric analysis is often of the greatest importance, as it solves questions which cannot be attacked by the usual eudiometric methods.

Let  $x$  represent the original volume, and  $x_1$  the unabsorbed residue of the first gas, in both cases reduced to the pressure 1; and, as before, let  $V_1$  be the volume of the unabsorbed gas under the pressure  $P_1$ .

The pressure of the unabsorbed portion of the first gas is then  $\frac{x_1}{V_1}$  and the volume of absorbed gas reduced to this pressure is  $\alpha h$ , or reduced to the pressure 1, it is  $\frac{x_1}{V_1} \cdot \alpha h$ .

Hence  $x = x_1 + \frac{x_1}{V_1} \cdot \alpha h$ ; and the pressure of the unabsorbed portion of the first is  $\frac{x_1}{V_1} = \frac{x}{V_1 + \alpha h}$ . In like manner, the pressure of the second gas is obtained, and we have the following expressions for the pressure before and after the absorption:

$$P = \frac{x}{V} + \frac{y}{V}; \quad P_1 = \frac{x}{V_1 + \alpha h} + \frac{y}{V_1 + \beta h}.$$

If we then set  $VP = W$ ;  $(V_1 + \alpha h)P_1 = A$ ;  $(V_1 + \beta h)P_1 = B$ , we have the volumes of the first and second gases in the unit-volume of the mixture, namely:

$$\frac{x}{x+y} = \frac{W-B}{A-B} \cdot \frac{A}{W}; \quad \text{and} \quad \frac{y}{x+y} = \frac{A-W}{A-B} \cdot \frac{B}{W}. \quad (2)$$

By help of these formulæ we can test the truth of Dalton's law; for if the result thus calculated agrees with those determined by experiment, the basis upon which the calculations are founded must be correct.

In order then to test the applicability of these formulæ, a mixture of carbonic acid and hydrogen was made, and the volume of each gas determined by eudiometric analysis; the gas was found to consist of:

Hydrogen . . . . .	26.81
Carbonic acid . . . . .	73.19
	<hr/> 100.00

An absorptiometric analysis of the same gas was then made, and by means of formula (2), the composition of the original gaseous mixture found to be:

Hydrogen . . . . .	26.67
Carbonic acid . . . . .	73.33
	<hr/> 100.00

The composition of the residual gas was found by direct analysis to be:

Hydrogen . . . . .	93.01
Carbonic acid . . . . .	6.99
	<hr/> 100.00

Or the partial pressure of the hydrogen was 0.5688 m., and that of the carbonic acid 0.04275 m.

The mean of three absorptiometric experiments gave as the composition of the residual gas, calculated according to formula (1):

Hydrogen . . . . .	91.64
Carbonic acid . . . . .	8.36
	<hr/> 100.00

or the partial pressure of the hydrogen was 0.6065 m., and that of the carbonic acid 0.0593 m.

From the close agreement between the results of the eudiometric and absorptiometric analyses, it is seen that Dalton's law holds good, at least for the two gases here considered. Many other gaseous mixtures have already been examined with a like

result; for the details of these experiments, we must, however, refer to the memoirs already cited.

There are, nevertheless, cases in which the constituents of a mixture of gases are not dissolved in liquids in the proportion required by the law of partial pressures, although no definite chemical combination occurs. Thus, for instance, Roscoe (Chem. Soc. Qu. J. viii. 14) has shown that mixtures of equal volumes of chlorine and hydrogen, and mixtures of varying proportions of chlorine and carbonic acid, do not dissolve in water in quantities proportional to the partial pressures of each gas. As, however, both hydrogen and carbonic acid have been shown to obey the law, the discrepancy can only arise from the chlorine. The mixture of equal volumes of chlorine and hydrogen was obtained perfectly pure and of constant composition, by the electrolysis of concentrated hydrochloric acid; and it was found that when water was saturated with this gas, the amount of chlorine dissolved was always much larger than that required by the law of partial pressures, as calculated from the coefficients of absorption and the relative volumes of the two gases; thus, at  $14^{\circ}$ , 9.834 grms. of water dissolved 14.70 volumes of chlorine, whereas the calculated quantity is only 11.65 volumes; and similarly for other temperatures. From a number of experiments, Roscoe concluded that no definite decomposition of the water by the chlorine takes place, which might possibly account for the increased solubility of that gas; and hence it appeared that, at temperatures not very far removed from the point at which a hydrate is formed (the experiments extended from  $13^{\circ}$  to  $38^{\circ}$ ), chlorine is retained by water with a force which, although not great enough to effect a definite combination, is sufficient to disturb the regular action of the law of absorption. The amount of this disturbance, that is, the quantity of chlorine contained in the liquid over and above that required by the law, can be easily calculated, and it has been shown that this amount, in the case of chlorine and hydrogen, diminishes with increase of temperature. In order to see whether this molecular disturbance is dependent upon the nature of the gas in contact with the chlorine, the solubility of mixtures of chlorine and carbonic acid was determined, and it appeared that an excess of chlorine above the quantity required by the law is dissolved, but that the amount of this chemically attached chlorine is, as far as the experiments reached, independent of changes of temperature, proving, therefore, that the amount of this molecular disturbing action depends on the nature of the gases or other substances present.

The limits of pressure beyond which gases do not obey the law of pressure, have not as yet been experimentally ascertained in many cases. It appears, however, that the law is not strictly applicable, at least, in the case of the more soluble gases, within ranges of pressure varying from 0 to 2 atmospheres. Thus, as has been stated, the quantity of ammonia absorbed by water under varying pressure differs very considerably from that required by theory; and this result was fully proved by experiments made by Mr. Sims in the writer's laboratory (Chem. Soc. J. xiv. 1). These experiments showed that under direct variation of pressure from 0.050 to 2.5 metres of mercury the quantity of ammonia dissolved in water at all temperatures below  $100^{\circ}$  C. is not directly proportional to the pressure; but that the deviation becomes less as the temperature increases, until at  $100^{\circ}$  C. the law of Dalton holds good. Similar results were obtained for sulphurous acid; this gas was shown to obey the law only at temperatures above  $50^{\circ}$  C. Further experiments on this subject, made at the writer's suggestion, by Mr. W. M. Watts, prove that admixture of ammonia with air produces the same effect on the solubility of that gas in water as a direct diminution of pressure.

When gases obeying Dalton's law are absorbed in a liquid, and this liquid is placed in conditions under which the pressure on the absorbed gases is reduced to 0, these gases escape in time completely from the liquid. This reduction of the pressure can be effected in many ways, either by actually removing all pressure, except that of the tension of the liquid, by evacuation under the receiver of an air-pump: or by placing the saturated liquid in an atmosphere of a gas different from any of those absorbed, whose volume may be regarded as infinite as compared with that of the absorbed gases; or lastly by bringing the liquid to its boiling point and continuing the ebullition, or what is the same thing, by passing a foreign gas or vapour through the liquid. In all these cases, the absorptiometric equilibrium is, after a certain time, established, and is dependent upon the partial pressures. From these considerations we see how impossible it is to keep a gas pure for any length of time when standing over a liquid in which it is ever so slightly soluble; thus, for instance, when hydrogen, one of the least soluble of the gases, is placed over water, a continuous interchange between the air outside, and the hydrogen inside, goes on through the medium of the water, the hydrogen dissolving and then escaping into the air where the partial pressure on it is 0, and the air in turn entering into the hydrogen, until an equilibrium in accordance with the pressures is established, which in this case only occurs when all the hydrogen has escaped and the vessel is filled with air.



This complete removal of absorbed gases by ebullition, or by contact with a foreign gas, does not occur in the case of most of those which are retained by the liquid with a greater degree of force than those obeying the law of pressures; thus, for instance, hydrochloric acid gas cannot be completely expelled from its aqueous solution by boiling or by passing air through the liquid. Water saturated at ordinary temperatures with hydrochloric acid gas, loses on heating more gas than water, until a certain point is reached, at which the gas and water distil over in constant proportions. For the ordinary atmospheric pressure, this constant ratio occurs at a temperature of  $110^{\circ}$ , when the distilled liquid contains 20.2 per cent. of anhydrous acid; this ratio is, however, dependent upon the temperature; when the temperature is diminished, the concentration of the residual acid is increased. Hence, under ordinary pressures, a solution containing less than 20 per cent. of acid must become more concentrated when boiled, and such is found to be the case, hydrochloric acid being in fact non-volatile when mixed with a certain quantity of water.\*

The solubility of *hydrochloric acid gas* in water at different temperatures, and under variation of pressure, has been determined by Messrs. Roscoe and Dittmar, (Chem. Soc. Qu. J., xii. 128). As might be expected, the amount of hydrochloric acid dissolved increases but slightly with increase of pressure. The following table gives the weight of this gas (G), which is absorbed by one gramme of water at  $0^{\circ}$  C. under the pressure (P) of mercury.

P.	G.	P.	G.	P.	G.	P.	G.
0.06 m.	0.613	0.30 m.	0.738	0.70 m.	0.817	1.10 m.	0.869
0.10	0.657	0.40	0.763	0.80	0.831	1.20	0.882
0.15	0.686	0.50	0.782	0.90	0.844	1.30	0.895
0.20	0.707	0.60	0.800	1.00	0.856		

The relation between the amount of dissolved hydrochloric acid gas and the temperature is seen from the appended numbers, giving the weight of gas absorbed under the normal pressure of 0.76 m.

$0^{\circ}$ C.	gm.	$16^{\circ}$	gm.	$32^{\circ}$	gm.	$48^{\circ}$	gm.
	0.825		0.742		0.665		0.603
$4^{\circ}$	0.804	$20^{\circ}$	0.721	$36^{\circ}$	0.649	$52^{\circ}$	0.589
$8^{\circ}$	0.783	$24^{\circ}$	0.700	$40^{\circ}$	0.633	$56^{\circ}$	0.575
$12^{\circ}$	0.762	$28^{\circ}$	0.682	$44^{\circ}$	0.618	$60^{\circ}$	0.561

Although not obeying the simple laws of absorption, hydrochloric acid gas does not, as Roscoe and Dittmar have shown, form any compounds with water which can be regarded as definite hydrates, the amount of absorbed gas varying with every change of physical circumstance. Roscoe has also shown (Chem. Soc. J. xiii. 146, and xv. 270) that the same law applies to the formation of all the hydrated acids of constant boiling point, none of which can be regarded as definite chemical compounds. For further information upon this subject we must, however, refer the reader to the original memoirs.

Although gases, as a rule, increase in solubility with diminution of temperature, yet it is found in most cases that the whole of the absorbed gas is liberated on the solidification of the liquid. Thus when water freezes, the whole of the dissolved air escapes in bubbles; and silver, which, according to Gay-Lussac, absorbs when melted about twenty times its volume of oxygen, expels it on solidifying, giving rise to the remarkable phenomenon of the "spitting" of silver. In the case of the liquefiable gases, however, such as carbonic acid, hydrochloric acid, and ammonia, no such expulsion of the gas on solidification of the liquid has been observed.

Many of the applications of these laws of absorption are both interesting and important; thus, instances occur in which eudiometric analysis by itself is unable completely to decide the composition of a gaseous mixture, as, for example, in the case of a mixture of equal volumes of methyl and hydrogen gases, which we cannot distinguish by combustion-analysis from marsh-gas; so that we are in uncertainty as to whether the gas evolved by the action of a hydrated alkali upon an acetate is really marsh-gas or a mixture of hydrogen and methyl. In this case, then, absorptiometric determinations are of the highest value; for in this way, by means of a single physical experiment, we are able to solve this doubtful question. The considerations and the formulæ already given, generally developed in Bunsen's memoir, render it possible to calculate from the absorptiometric data, the composition of an unknown gaseous mixture: that is to say, to determine at the observed temperature the coefficients of the absorbed

\* The vapour of water acts precisely as a foreign gas would do in reducing the partial pressures; hence in all the calculations of the absorption-coefficients of gases in liquids determined chemically, the vapour of water present in the atmosphere of otherwise pure gas existing above the liquid must be regarded as a foreign gas, which therefore alters the pressure on the absorbed gases. This consideration has been attended to in but few of the chemical determinations yet made of the more soluble gases.

and the partial pressures of the unabsorbed gases. If, then, with the data afforded by the absorption of the gas of the acetates, the coefficients are calculated, on the assumption that the gas consists of a mixture of equal volumes of hydrogen and methyl, it is found that the sum of the coefficients has a negative value, instead of being equal to the sum of the two numbers given in the tables for methyl and hydrogen. If, on the other hand, the calculation is based on the supposition that the gas from the acetates is not a mixture but a single gas, the value found for the coefficient by calculation is identical with that determined for true marsh-gas at the observed temperature. Hence we may conclude that the gas prepared from the acetates is neither a mixture of methyl and hydrogen, nor a substance isomeric with marsh-gas, but that it is actually the same body that issues from the mud-volcanoes in the Crimea.

The same degree of uncertainty prevails respecting the identity of chloride of methyl when prepared in different ways. Baeyer (Ann. Ch. Pharm. c. iii. p. 181) has, however, lately shown that the substance prepared by heating cacodylic and hydrochloric acids has exactly the same coefficient of absorption in water as the chloride of methyl prepared in the ordinary way from wood-spirit by chloride of sodium and sulphuric acid, whilst the solubility of the compound prepared by the union of marsh-gas and chlorine in diffused light is totally different. Hence Baeyer concludes that the two first are identical, and that these two are distinct substances from the third. [Berthelot, however (Compt. rend. xlv. 916), has made other experiments from which he concludes this third substance is also a true chloride of methyl.]

Many other interesting deductions from, and applications of, the laws of absorption have already been made, for the details of which we must again refer to the original memoirs. Thus, by means of the formulæ previously developed, the composition of the gases absorbed in the water of a mineral spring can be calculated from the composition of the free gas which escapes from the water, or *vice versa*. In all cases, in fact, in which a statical equilibrium between the absorbed and free gases can occur, these calculations are applicable; and in none more so than in the composition of the gases contained in rain and dew. The composition of the atmosphere we may take to be:

Oxygen	:	:	:	:	:	:	20.9512
Nitrogen	:	:	:	:	:	:	79.0073
Carbonic acid	:	:	:	:	:	:	0.0415
							100.0000

From these numbers, and from the coefficients of the three gases, Bunsen obtained by calculation the following composition of the gases contained in rain-water.

	0°	5°	10°	15°	20°
Nitrogen . . .	63.20	63.35	63.49	63.62	63.69
Oxygen . . .	33.88	33.97	34.05	34.12	34.17
Carbonic acid . .	2.92	2.68	2.46	2.26	2.14
	100.00	100.00	100.00	100.00	100.00

A very important extension of these laws of absorption has lately been made in an investigation upon the gases of the blood carried out by Lothar Meyer.\* This chemist collected the gases dissolved in the blood by boiling the diluted blood in a vacuum space, according to the method described by Bunsen in his gasometry, and liberated the portion of the carbonic acid which is combined with the alkalis of the blood by adding tartaric acid to the blood before boiling. In 100 vols. of blood, Meyer found the following volumes of gas reduced to 0° and 0.76:

Description of Blood.	Free Gas.	O.	N.	Free CO <sub>2</sub> .	Combined CO <sub>2</sub> .	Total CO <sub>2</sub> .	Total volume of gas
Carotid artery, Dog. No. 2.					23.75		
" " " 1.	20.88	12.43	2.83	5.62	28.61	34.23	49.49
" " " 2.		(3.79)	(2.94)			(27.10)	(33.84)
" " " 1.	28.24	18.42	4.55	5.28	20.97	26.25	49.21
" " " 1.	25.60	14.29	5.04	6.17	28.58	34.75	54.08
Defibrinated blood shaken with air at 25° and 0.7463m.	17.04	11.55	4.40	1.09	18.12	19.21	35.16
		(5.81)	(4.12)			(21.56)	(31.49)

\* Abstract of paper in Phil. Mag. (4) xiv. 263. The original memoir is found in Henle and Pfeuffer's Zeitschrift für rationelle Medicin. Neue Folge, viii. 256.

In order to obtain the coefficients of absorption of defibrinated blood for various gases, Meyer employed an apparatus somewhat different from the one used by Bunsen. It appears from his experiments that the amounts of carbonic acid, oxygen, and nitrogen absorbed in the blood, vary with the pressure, but that whereas the whole of the nitrogen obeys the law of natural pressures, only a portion of the carbonic acid and the oxygen does so; that is, in the case of both these gases, one portion of the dissolved quantity is more forcibly retained by the blood than the other, and is independent of changes of pressure, exactly as has been shown to be the case with chlorine and water. The amount of this attached oxygen is far larger than the truly absorbed portion; and from these facts we may draw the interesting conclusion that the richness or poverty of a given volume of air in oxygen, at various heights above the sea level for instance, can exert but a very slight influence on the total volume of oxygen contained in the blood, and therefore upon animal life.

II. *Absorption of Gases by Solids.*—Porous carbon in the form of charcoal is the only solid substance whose coefficients of absorption for various gases have been determined with any approach to accuracy. From the experiments of Saussure, made with the charcoal of box-wood, it appears that 1 volume of charcoal absorbs, at 12° C. and under a pressure of 724 millimetres of mercury, the following volumes of gas:

	Volumes.		Volumes.
Ammoniacal gas . . . .	90	Olefiant gas . . . .	35.0
Hydrochloric acid gas . .	85	Carbonic oxide . . . .	9.4
Sulphurous acid . . . .	65	Oxygen . . . .	9.4
Sulphuretted hydrogen . .	55	Nitrogen . . . .	7.5
Nitrous oxide . . . .	40	Hydrogen . . . .	1.75
Carbonic acid . . . .	35		

The absorption which several other solid bodies, such as gypsum, meerschaum, woods of various kinds, wool, silk, &c., effect upon gases has also been determined by Saussure, but from the indefinite nature of the substances operated upon, the numbers obtained have but slight interest. Later experiments of Favre (*Compt. rend.* xxxix. 729) confirm Saussure's results, in so far, at least, as concerns the order of solubility in which the gases are arranged.

The coefficients above given represent the quantity of gas taken up by one volume of charcoal previously freed from any foreign gas absorbed in the pores. This purification of the charcoal can only be effected by a high temperature, for it has been shown that the simple removal of the atmospheric pressure by no means expels all the gas previously absorbed. Whether the whole of the absorbed gas is expelled at a red heat is as yet an unascertained matter; but it is known that much more gas is thus driven off than can be removed by the mere withdrawal of the atmospheric pressure, and hence we see that, at a high temperature, the attraction of the particles of solid and gas effecting the absorption is, if not altogether destroyed, at any rate much diminished. When a solid body is brought into an atmosphere consisting of a mixture of different gases, each one of the several gases will be absorbed in quantities dependent upon the relative amount of that gas present and its particular coefficient of absorption. Thus, for example, a piece of charcoal, or any other solid, exposed to the air, absorbs a definite quantity of nitrogen, oxygen, carbonic acid, and aqueous vapour, which thus lose their gaseous elasticity or tension, become in fact solid, and can be removed only with great difficulty. Dr. R. Angus Smith has quite recently communicated the results of some experiments upon the solubility of certain gases in charcoal (*Proc. Roy. Soc.* xii. 424), the most important points of which he summarises in the following sentences:

1. Charcoal absorbs oxygen so as to separate it from common air, or from its mixtures with hydrogen and nitrogen at common temperatures.
2. Charcoal continues the absorption of oxygen for at least a month, although the chief amount is absorbed in a few hours, sometimes in a few seconds, according to the quality of the charcoal.
3. It does not absorb hydrogen, nitrogen, or carbonic acid for the same period.
4. Although the amount absorbed is somewhat in the relation of the condensability of the gases by pressure, this is not the only quality regulating the absorption, of oxygen at least.
5. When it is sought to remove the oxygen from charcoal by warmth, carbonic acid is formed, even at the temperature of boiling water, and slowly even at lower temperatures.

Although, from the complicated nature of the modifying conditions, we are as yet acquainted with but few exact quantitative relations concerning the absorption of gases by solid bodies, still there are many interesting proofs of the existence of this absorption, even in the case of solids whose surface is small in comparison with their bulk.



Thus, for example, in the manufacture of exact barometers, great difficulty is experienced in separating from the interior of the tube the adhering or absorbed air, which, if not completely expelled, gradually resumes the gaseous condition, and entering into the Torricellian vacuum, renders the instrument incorrect. Thus, too, in the chemical photometer used by Bunsen and Roscoe, in which a perfectly pure mixture of equal volumes of chlorine and hydrogen is employed as the sensitive substance, the only conceivable reason why the chlorine and hydrogen must be passed for several days through the apparatus before the maximum and permanent degree of sensibility is reached, is that the oxygen and nitrogen absorbed by the glass is expelled with the greatest difficulty, and that (as proved by direct experiment) the most minute trace of foreign gas disturbs the action of the light to an immense extent. Similar effects produced by the layer of air which covers all solid bodies are well known to photographers, who carefully guard against the presence of this condensed atmosphere, removing it by mechanical means immediately before the plate receives the sensitive coating. Almost the whole of the singular phenomena, first investigated by Moser, and ascribed by him to the action of "latent light," may be more rationally explained by the application of the authenticated facts of the absorption of gases by solid bodies. The well-known experiment, for instance, of allowing a coin to remain for a short time on a freshly cleaned and brightly polished metallic plate, when, on removing the coin and breathing on the plate, the image is plainly seen, depends upon the absorptive action which the newly cleaned surface of the plate exerts upon the condensed gases of the coin; if the surface both of the plate and of the coin be equally saturated with gas no such image will be perceived, and if both be equally free from any condensed atmosphere, the same negative result will be obtained.

Many of the so-called "catalytic" actions which various metals produce upon gases may also be explained in a similar manner. The effect which finely divided platinum, or even a clean plate of that metal, exerts in producing the combination of oxygen and hydrogen, doubtless depends on the absorption of these gases on the surface of the platinum, the consequent approximation of the gaseous particles being sufficient to induce their chemical union, thus evolving heat enough to cause the combustion of the surrounding gas. The most definite, and therefore the most interesting, experiments on this subject have been made by Magnus (Pogg. Ann. lxxxix. 604). He has not only shown that, owing to the absorption of gases by solids, the coefficients of expansion of gases by heat differ when the extent of surface of the vessel in which they are confined is altered, but he has actually determined the quantity of gas absorbed by a square millimetre of glass. Thus in two vessels, the relation of whose surfaces (the capacity being the same) was as 1 to 36, the coefficients of expansion of sulphurous acid from  $0^{\circ}$  C. to  $100^{\circ}$  C. were 0.3822 and 0.3896 respectively, or the amount of sulphurous acid absorbed on each square millimetre of surface was 0.0008 cubic millimetre. The same result was obtained when spongy platinum was placed in the gas: without spongy platinum the coefficient of expansion of sulphurous acid was found to be 0.3832, and in presence of the finely divided metal, 0.3922. It is more than probable that in Regnault's classical researches upon the action of pressure on gases, a portion of the deviation which in every case was observed from the law of Mariotte, was due to this condensation of the gas upon the surfaces of the enclosing vessels. In the exact determination of gaseous specific gravities, these absorptive phenomena also exert a disturbing influence.

H. E. R.

**GASES, COLLECTION AND PRESERVATION OF.** There are three general methods of collecting gases, the choice between which must depend upon the manner in which the gas is generated, and the degree of purity required by the use to which it is to be applied.

1. *By reception in an exhausted vessel.*—A vessel of glass or metal, provided with a stopcock, is exhausted as completely as possible by the air-pump, and then connected with the reservoir containing the gas.

This method is not of very frequent application, partly because it requires somewhat complicated apparatus, and partly from the impossibility of obtaining a complete vacuum with the air-pump. When, however, the supply of gas is unlimited, as when samples of air are to be collected from different localities for analysis, it answers very well; because the vessel, after having been once exhausted and filled with the gas, may be exhausted again and re-filled, and this operation repeated till every trace of the air originally contained in the vessel is removed.

A method similar in principle, and often very convenient, especially for lecture experiments, is to collect the gas in a bladder or caoutchouc bag, provided with a stopcock, and previously emptied of air by pressure. Larger quantities of gas, such as are required for the oxy-hydrogen blowpipe, may be collected in large linen bags coated on both sides with caoutchouc. The bags when full are connected by flexible

tubes with the nozzle of the blow-pipe, and the gases are pressed out by laying weights upon the bags, placed for the purpose between boards.

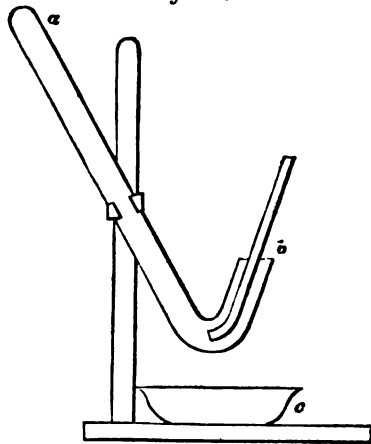
2. *By displacement of the air.*—To fill a vessel in this manner with a gas heavier than the air, such as chlorine, hydrochloric acid, or carbonic anhydride, the delivery-tube proceeding from the generating vessel is made to pass down to the bottom of the receiver, placed with its mouth upwards. The gas then gradually fills the vessel, driving out the atmospheric air at the top. The operator judges when the vessel is full of gas, in the case of chlorine, by the colour; in the case of acid gases, by the reddening of litmus held over the mouth of the vessel; and in the case of carbonic anhydride, by the rapid extinction of a lighted taper held there. For gases lighter than air, such as hydrogen and ammonia, the generating vessel is fitted with an upright delivery-tube, and the vessel in which the gas is to be collected is inverted and held over it, with the end of the delivery-tube reaching quite to the top of the vessel. This method is especially convenient for collecting large quantities of gases which are quickly absorbed by water, or when a considerable quantity of gas is required in the dry state.

3. *Collection over liquids.*—The mode of collection which is applicable in the greatest number of cases, is to receive the gas over a liquid which will not absorb it, the liquids most frequently used for the purpose being water or mercury. A jar or bottle is filled with the liquid and inverted in a trough of the same, and the end of the delivery-tube proceeding from the gas-generating apparatus is inserted beneath the mouth of the jar, so that the gas may rise in bubbles through the liquid, displace it, and fill the vessel. The method is too well known to need more particular description. If a gas not absorbed by water is to be kept, it is collected in a bottle in the manner just indicated, and the bottle, when nearly full, is closed, while still standing in the trough, with a cork or ground stopper, then placed with its mouth downwards in a small basin containing sufficient water to cover the mouth. Or the bottle may be quite filled with the gas and closed with a greased stopper, afterwards tied down; or with a closely-fitting cork, which is afterwards covered and fastened down with sealing-wax, or tied round with bladder or sheet caoutchouc.

The methods of collecting and transferring gases over the mercurial trough for audiometric analysis are described in the article ANALYSIS OF GASES (i. 268).

An excellent substitute for a mercurial, and even for a water trough, in many

Fig. 510.



experiments, is the instrument known as *Cooper's mercurial receiver*. It consists of a glass tube, *a, b* (fig. 510), closed at one end and bent upwards. It is filled with mercury by inverting it and pouring in the mercury at *b*. On again inverting it, as in the figure, the mercury is retained in the tube by the pressure of the atmosphere. On inserting the delivery-tube at *b*, gas enters and displaces the mercury, which is received in the basin *c*. The operation must be stopped when the tube is filled with gas to the bend.

The apparatus affords great facilities for making a number of experiments on a small quantity of gas; for by placing the thumb on the end *b*, and inclining the tube so as to allow a little of the gas to flow round the bend into the short arm, it may be examined as to its chemical or physical characters, such as smell, inflammability, reaction with test-papers, &c. (*Greville Williams's Chemical Manipulation*, p. 320.)

For collecting and preserving large quantities of gases not absorbed by water, vessels called gas-holders or gasometers are frequently employed. The most convenient form of gas-holder is that invented by Pepys, and represented in fig. 511. It consists of a drum or reservoir, *a*, of sheet copper, surmounted by a shallow trough or cistern, *n*, the communication between the two being made by a couple of tubes furnished with cocks, *g, h*, one of the tubes passing nearly to the bottom of the drum. A short wide open tube, *i*, is inserted obliquely near the bottom of the vessel, into which a plug may be tightly screwed. A glass water-gauge, *e, f*, affixed to the side of the drum, and communicating with both top and bottom, indicates the level of the liquid within. Sometimes a divided scale is attached to this tube to measure the in- and out-flow of the gas.

To use the gas-holder, the plug is first to be screwed into the lower opening, and

the drum completely filled with water. All three stopcocks are then to be closed, and the plug removed. The pressure of the atmosphere retains the water in the gas-holder, and if no air-leakage occurs, the escape of water is inconsiderable. The extremity of the delivery-tube is now to be well pushed through the open aperture into the drum, so that the bubbles of gas rise without hindrance to the upper part, displacing the water, which flows out in the same proportion into a vessel placed for its reception. When the drum is filled, or enough gas has been collected, the tube is withdrawn, and the plug screwed into its place.

When a portion of the gas is to be transferred to a jar, the latter is to be filled with water at the pneumatic trough, carried by the help of a basin or plate to the cistern of the gas-holder, and placed over the shorter tube. On opening the cocks of both tubes, water will flow down the longer tube into the drum, and force the gas through the shorter tube into the jar. The vessel when filled may again have the plate slipped under it and removed.

This gas-holder is very convenient for passing a stream of gas over any substance contained in a tube or other vessel, as in experiments of oxidation and reduction. For this purpose, the vessel containing the substance to be operated upon is connected air-tight with the cock *c* of the gas-holder, and the cocks *c, g* are opened. The pressure of the water then forces the gas through the tube. In the same manner a bladder may be filled with gas by attaching it to the stopcock *c*. If great pressure is required, a long tin tube, terminating in a funnel, may be screwed into the upper end of the long tube of the gas-holder, and water poured in at the funnel.

The gas-holder may also be used as an aspirator, by filling it with water, closing the cocks *g, h*, connecting the vessel through which the air is to be drawn with the cock *c*, and opening the plug. The water then runs out, and its place is supplied by air.

Another form of gas-holder or gasometer, more used in manufacturing operations than in the laboratory, consists of two metal cylinders, (*fig. 512*) one inverted within the other, which contains water. The inner cylinder *A* is counterpoised by weights, *w*, passing over pulleys, so that it will easily move upwards when pressed from below. A metal tube, *cde*, provided with a stopcock, *s*, passes through the side of the outer cylinder close to the bottom, then vertically upwards to within a short distance of the top of the inner cylinder when in its lowest position.

To use this apparatus, the stopcock *s* is opened, the inner cylinder depressed to its lowest position, and water poured into the outer vessel till it fills the inner one, driving the air before it through the open tube. The outer extremity *c* of this tube being then connected with the delivery-tube proceeding from the generating vessel, the gas enters, passes upwards, and pushes up the inner cylinder, which is thus gradually raised to its highest position, and filled with gas. The stop-cock is then closed. To transfer the gas, a delivery-tube is attached to the end *c* of the tube *cde*, the stopcock is opened, and a portion of the weight which counterpoises the inner cylinder is removed. This cylinder then descends by its own weight, driving the gas before it through the tube *cde*. The flow may be made slow or rapid by removing less or more of the counterpoise.

This form of gas-holder is equally convenient with that of Pepys for passing a continuous stream of gas through a tube or vessel; but it does not afford the same facility of filling jars or bottles with gas.

For figures of the large gasometers used in gas-works, see *Ure's Dictionary of Arts*, art. COAL-GAS (i. 749-763).

Gases required to be preserved in a state of purity must not, however, be left standing over water; for water absorbs the gases of the external atmosphere, and these dissolved gases afterwards diffuse themselves into the gas standing over the water (p. 801); moreover, as all gases are more or less soluble in water, each to an extent peculiar to itself, the composition of a gaseous mixture standing over water, necessarily undergoes alteration in course of time.

Fig. 511.

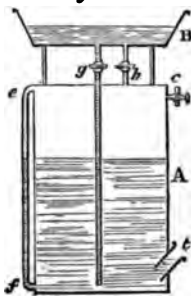
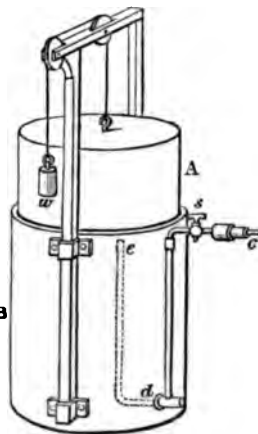


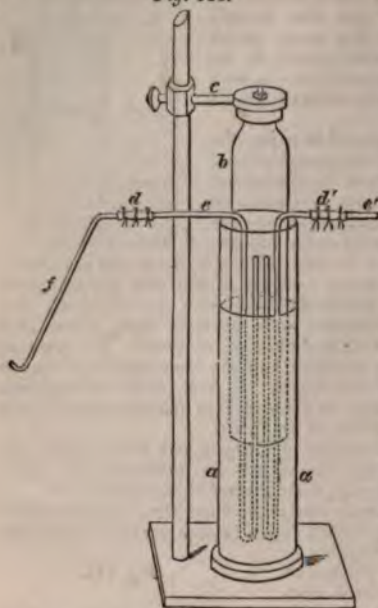
Fig. 512.





To avoid this source of error, and at the same time to obtain an apparatus which gives facility for withdrawing successive samples of a gaseous mixture for examination, Bunsen has contrived the mercurial gasometer represented in *fig. 513*. Its construction

*Fig. 513.*



is exactly similar to that of the common gasometer last described. The outer cylinder, *aa*, is filled with mercury, and the bell-jar, *bb*, can be moved up and down in it by means of the holder *c*. The delivery and exit tubes, *e, e'*, are bent in the V shape, and pass under the bell-jar; to the outer end of each of them is attached a caoutchouc tube, *d, d'*, within which is placed a small piece of glass-rod, fitting it loosely, so as to afford easy passage for a gas, but forming a perfectly air-tight joint when the caoutchouc tube is tied round it with a silk cord. When the bell-jar is to be filled, it must be sunk as far as possible in the cylinder *aa*, care being taken that the tubes *e, e'*, do not dip under the mercury. As soon as the air has been completely displaced by the current of gas, the valve *d* is closed, the bell-jar drawn out of the mercury as it fills, and when this is accomplished the valve *d'* is also closed. To take a sample of the gas thus collected, a capillary gas-delivery-tube, *f*, filled with mercury, is fixed air-tight into the closed caoutchouc valve *d*, and the end of the delivery-tube being placed under the vessel to which the gas is to be transferred—a endiometer, for example—in the mercurial trough, the valve *d* is slowly opened; the bell-jar then descends by its own weight, and forces the gas through the tube.

If the nature of the investigation requires the transference of a given volume of gas without loss, the vessel represented in *figs. 37, 38, 39*, (pp. 243, 244, vol. i.), or one of similar construction, but with a cylindrical body and having a divided scale marked on it, may be used. (See *Bunsen's Gasometry*, p. 20.)

*Preservation of gases in sealed tubes.*—In researches on the nature of the gases evolved in manufacturing operations or from natural sources, such as volcanic fissures, clefts in mines, spring-waters, or samples of air from particular localities, it is frequently necessary to keep the gases for some time, and transport them to a distance before they can be analysed; and the only way of securing them absolutely from alteration, or from admixture with air, is to receive them in vessels which can be hermetically sealed. Bunsen has contrived for this purpose a number of highly ingenious methods, which are fully described in his "*Gasometry*."

If the gas issues under pressure, a number of tubes 5 or 6 inches long, about  $\frac{3}{4}$  of an inch wide, and drawn out at each end, so as to be quickly and easily sealed by the blowpipe, are connected together by caoutchouc tubes, and the gas is made to flow through the whole arrangement long enough to drive out all the atmospheric air. The outer extremities of the first and last tubes are then sealed by the blowpipe; afterwards the necks of the intermediate tubes in succession, so as to separate them, and enclose a quantity of the gas in each. It was by an arrangement of this kind that Bunsen collected the gases from blast-furnaces for analysis. A wide wrought iron tube, consisting of several pieces screwed together, was sunk in the furnace, and the gases, forced through it by the blast, were conveyed by a flexible leaden pipe into a series of glass tubes connected as above.

If the pressure under which the gas issues from its source is not sufficient to drive it through the series of glass tubes, it must be drawn through them by an exhausting syringe or an aspirator. This is sometimes the case with the gas which issues from clefts in coal strata or from volcanic fissures. To collect such gases, the series of narrow tubes is connected at one end with a long wide tube of lead or glass, which can be inserted into the fissure, and at the other end with the syringe, which is worked long enough to ensure the complete expulsion of atmospheric air from the apparatus. The tubes are then sealed and separated as before.

For collecting gases in situations easy of access, as for instance in researches on the

composition of the atmosphere, or of the air of mines and caves, a common flask of a capacity of from 2 to 16 ounces, and having its neck drawn out to a narrow tube at the distance of  $\frac{3}{4}$  of an inch from the mouth, may be used. To fill this bottle with the gaseous mixture of the locality, the air is sucked out of it through a long tube, reaching to the bottom, five or six deep inspirations being sufficient for the purpose; after which, the flask is closed with a cork, and the neck sealed by the blowpipe flame.

Gases evolved under water, like marsh-gas from stagnant pools, or the gases from springs, may be collected by means of the apparatus represented in *fig. 514*. It consists of a small test-tube having a capacity of 40 to 60 cubic centimetres, drawn out before the blowpipe at *a* to the thickness of a straw, and fixed by a cork or a vulcanised caoutchouc tube to the funnel *b*. Instead of the test-tube, a small long-necked flask may be used, having its neck similarly drawn out before the blowpipe. The apparatus is first filled with the water by immersing it with the mouth of the funnel upwards; but as the water is thus brought in contact with the air, which will alter the composition of the gases absorbed by the water, the water must be sucked out of the apparatus through a small tube reaching to the lowest part, till the whole has been displaced by other water from the spring. The apparatus may then be inverted, and the gas suffered to rise into the tube. If the bubbles stop in the neck of the funnel, or in the narrow part of the tube, they may be made to ascend by tapping the edge of the funnel against any hard substance.

When the tube is full of gas, the apparatus may be removed from the spring by means of a small basin, and the tube melted off at *a* by the blowpipe, the moisture at that part having been previously expelled by the flame. The column of water which rises in the funnel above the level of the water in the basin, renders the pressure on the gas less than that of the atmosphere; hence no bulging of the tube can take place. (Bunsen.)

Fig. 514.

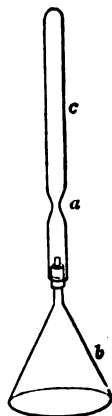
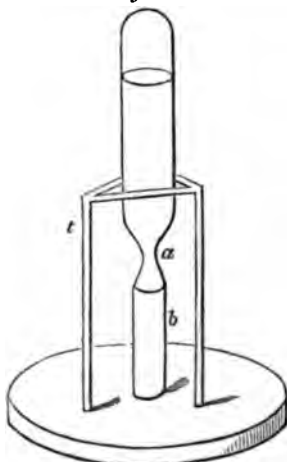


Fig. 515.



Another way of mounting an apparatus for collecting gases from springs is that adopted by Hofmann in the examination of the Harrogate waters (*Chem. Soc. Qu. J. vii. 169*). In this apparatus (*fig. 515*), the tube, narrowed in one part, *a*, as above, is supported on an iron tripod *t*, and fixed by means of a strong caoutchouc connector *b*, into a large perforated wooden float, the lower surface of which is hollowed out so as to collect the gas-bubbles, and cause them to ascend into the receiver, which is filled with water at the commencement of the operation. As soon as the receiver is filled, the caoutchouc connector is closed by means of a screw-clamp, and the receiver is disconnected and sealed before the blowpipe. For the method of collecting the gases dissolved in waters, see *WATERS, MINERAL*.

**GASES, COMBINATION OF, BY VOLUME.** The specific gravities of elementary bodies in the gaseous state are to one another, for the most part, in the same ratio as their atomic weights; thus the volume which corresponds to any given quantity, say 1 gramme of hydrogen, corresponds also to 14 grammes of nitrogen, 16 grammes of oxygen, 32 grammes of sulphur-vapour, 35.5 grammes of chlorine, 80 grammes of bromine, and 127 grammes of iodine, so that the specific gravities, or weights of equal volumes, of these elements in the gaseous state, referred to hydrogen as unity,

are expressed by the same numbers as their atomic weights; and the symbols H, N, O, Cl, Br, &c., which represent the atomic weights, likewise represent equal volumes of the several gases.

The exceptions to this law are the following:—1. The specific gravities of phosphorus and arsenic in the state of gas or vapour are twice as great as their atomic weights ( $P = 31$ ,  $As = 76$ ), so that their atoms in the gaseous state occupy only half the volume of an atom of hydrogen. To bring these elements under the general law, it would be necessary to double their atomic weights, to which, however, there are grave objections.

2. The vapour-densities of mercury and cadmium accord with the atomic weights given in the table at page 466, vol. i.; but if the atomic weights of these elements are doubled, for which there appear to be conclusive reasons (see CLASSIFICATION, i. 1008, footnote), their atoms in the gaseous state will occupy twice the volume of an atom of hydrogen. The duplication of their atomic weights would, in fact, bring these metals into accordance with the majority of diatomic radicles, the atoms or smallest combining weights of which occupy, in the gaseous state, twice the volume of those of monatomic radicles\*; e. g.

Monatomic radicles.  
1 at. =  $\frac{1}{2}$  molecule = 1 vol.

H  
CH<sup>3</sup>  
C<sup>2</sup>H<sup>4</sup>  
C<sup>3</sup>H<sup>8</sup>  
&c.

Diatomic radicles.  
1 at. = 1 molecule = 2 vol.

Cd<sup>2</sup>  
Hg<sup>2</sup>  
C<sup>2</sup>H<sup>4</sup>  
C<sup>2</sup>H<sup>6</sup>  
&c.

From the preceding relations, it follows that the volumes of any two elementary gases which make up a compound molecule, are to one another in the same ratio as the numbers of atoms of the same elements which enter into the compound, excepting in the case of phosphorus and arsenic, for which the number of volumes thus determined has to be halved, and of mercury and cadmium, for which it should probably be doubled: thus:—

The molecule	HCl	contains	1 vol. H	and 1 vol. Cl
"	H <sup>2</sup> O	"	2 " H	" 1 " O.
"	H <sup>2</sup> N	"	3 " H	" 1 " N.
"	H <sup>2</sup> P	"	3 " H	" $\frac{1}{2}$ " P.
"		{ or 6 " H	" 1 " P.	
"	Cl <sup>2</sup> As	"	3 " Cl	" $\frac{1}{2}$ " As.
"		{ or 6 " Cl	" 1 " As.	
"	Hg <sup>2</sup> Cl <sup>2</sup>	"	2 " Hg <sup>2</sup>	" 2 " Cl.

If the smallest volume of a gaseous element that can enter into combination be called the combining volume of that element, the law of combination may be expressed as follows:—*The combining volumes of all elementary gases are equal, excepting those of phosphorus and arsenic, which are only half those of the other elements in the gaseous state, and probably also those of mercury and cadmium, which are double those of the other elements.*

It will of course be understood that the law, as thus stated, is true only for the atomic weights adopted in this work; according to the older system (that of *Gmelin's Handbook*), in which the atomic weights of oxygen and sulphur have only half the values here adopted, the combining volumes of those elements are likewise equal to those of phosphorus and arsenic.

But whichever system of atomic weights be adopted, the volumes in which gaseous elements combine together may be expressed by very simple numbers. This is the "Law of Volumes," first observed by Humboldt and Gay-Lussac in 1806, with regard to the combination of oxygen and hydrogen, and afterwards established in other cases by Gay-Lussac, whose observations published in his *Theory of Volumes*†, shortly after the announcement of the Atomic Theory by Dalton, afforded new and independent evidence of the combination of bodies in definite and multiple proportions, in corroboration of that derived from the observed proportions of combination by weight.

Gay-Lussac likewise observed that the product of the union of two gases, when itself a gas, sometimes retains the original volume of its constituents, no contraction or change of volume resulting from the combination, but that when contraction takes place, which is the most common case, the volume of the compound gas always bears a simple ratio to the volumes of its elements.

\* If this be really the general law of the vapour-volumes of diatomic radicles, the elements O, S, Se, and Te, whose vapour-volumes accord with that of hydrogen, must be regarded as exceptional.

† "Sur la combinaison des substances gazeuses les unes avec les autres."—*Mémoires d'Arcueil*, ii. 207 (1809).



Subsequent observation extended over a very large number of compounds, organic as well as inorganic, has shown that, with a few exceptions, probably only apparent, the molecules of compound bodies in the gaseous state occupy twice the volume of an atom of hydrogen gas. No matter what may be the number of atoms or volumes that enter into the compound, they all become condensed into two volumes: thus

1 vol.	H	and	1 vol.	Cl	form	2 vol.	HCl.
1 "	N	"	1 "	O	"	2 "	NO.
2 "	H	"	1 "	O	"	2 "	H <sup>2</sup> O.
3 "	H	"	1 "	N	"	2 "	H <sup>2</sup> N.
3 "	H	"	$\frac{1}{2}$ "	P	"	2 "	H <sup>2</sup> P.

Similarly in the union of compound gases, *e.g.*

1 vol.	ethyl,	C <sup>2</sup> H <sup>4</sup>	and	1 vol.	Cl	form	2 vol.	C <sup>2</sup> H <sup>4</sup> Cl.
2 "	ethyl,	C <sup>2</sup> H <sup>4</sup>	"	1 "	O	"	2 "	(C <sup>2</sup> H <sup>4</sup> ) <sup>2</sup> O.
2 "	ethylene,	C <sup>2</sup> H <sup>4</sup>	"	2 "	Cl	"	2 "	C <sup>2</sup> H <sup>4</sup> Cl <sup>2</sup> .
2 "	ethylene,	C <sup>2</sup> H <sup>4</sup>	"	1 "	O	"	2 "	C <sup>2</sup> H <sup>4</sup> O.

Hence it follows that the specific gravity of any compound gas or vapour, referred to hydrogen as unity, is equal to half its molecular weight.

The exceptions to this law have already been considered in the article *ATOMIC WEIGHTS* (i. 467-470). Those in which the observed vapour-density is less than that determined by calculation, according to the rule just given, may be explained by supposing that, at the high temperature at which the specific gravity of the vapour is determined, the compound molecule splits up into two others, *e.g.* NH<sup>2</sup>Cl into NH<sup>2</sup> + HCl (which subsequently recombine, as the temperature falls), so that we are really operating, not on one compound molecule, but on two of less complexity, whence the observed density corresponds to four volumes of vapour instead of two. The validity of this explanation has been experimentally demonstrated in the case of hydrate of diethyl-ethylene-diamine, C<sup>2</sup>H<sup>4</sup>N<sup>2</sup>.H<sup>2</sup>O, by Hofmann (p. 588); and the experiments of Pebal on sal-ammoniac, and of Wanklyn and Robinson on monohydrated sulphuric acid and pentachloride of phosphorus, which will be described hereafter (p. 817), point to the same conclusion. On the other hand, the recent experiments of Deville and Troost (*Ann. Ch. Pharm.* cxxvii. 274) throw considerable doubt upon the reality of these supposed decompositions and recompositions, at least in the case of ammoniac-salts. These chemists find indeed: 1. That sal-ammoniac bears without decomposition a temperature at which free ammonia is in great part resolved into its elements, and that when the heat is raised high enough to decompose the salt, the result is a mixture of hydrochloric acid, hydrogen, and nitrogen; moreover, a mixture of these three gases passed through a tube heated to dull redness, does not form sal-ammoniac. Bromide and iodide of ammonium yield similar results.—2. Cyanide of ammonium, which is produced at 1000° C. by the action of ammonia on charcoal, cannot be resolved into prussic acid and ammonia at 100° C., though at that temperature its vapour-density corresponds to a four-volume condensation.—3. Hydrochlorate of ethylamine is not resolved by heat into ammonia and chloride of ethyl; neither can it be produced by the direct union of those two gases.

With regard to those cases in which the observed density of the compound gas or vapour is greater than it should be according to calculation, it has been found that some of the exceptions arise from the vapour actually exhibiting a greater density at temperatures not far above the boiling point of the liquid, than at temperatures high enough to bring it into that state in which its physical properties agree in all respects with those of permanent gases. This has long been known to be the case with acetic acid and a few of its homologues, viz. formic, butyric and valerianic acids, and the same anomaly has recently been demonstrated by Playfair and Wanklyn (*Chem. Soc. J.* xv. 156), in the case of pernitric oxide, NO<sup>2</sup>, which at 97.6° C. has a density of 1.783 (air = 1) whereas at 24.5° it is 2.52, and at 11.3°, it is 2.69. The first of these densities corresponds nearly with the formula NO<sup>2</sup>, the latter approximates to that required by N<sup>2</sup>O<sup>4</sup>: for NO<sup>2</sup> gives  $\frac{46}{2} \times 0.0693 = 1.593$ ; and N<sup>2</sup>O<sup>4</sup> gives  $\frac{92}{2} \times 0.0693 = 3.188$ . Hence it would appear that, at all the temperatures observed, the gas is a mixture of two polymeric compounds, and at 100° C., or above, it consists for the most part of NO<sup>2</sup>.

The vapour-densities of mercuric chloride, ethylide of mercury, ethylide of zinc, and methylide of zinc, which correspond to 1 vol. of vapour of their molecules, as represented by the formulae HgCl, C<sup>2</sup>H<sup>4</sup>Hg, C<sup>2</sup>H<sup>4</sup>Zn, CH<sup>3</sup>Zn, respectively, become normal and correspond to 2 vols. if the atomic weights of mercury and zinc are doubled, as is now generally done, and these molecules are accordingly represented by the formulae Hg<sup>2</sup>Cl<sup>2</sup>, C<sup>2</sup>H<sup>4</sup><sup>2</sup>Hg<sup>2</sup>, C<sup>2</sup>H<sup>4</sup><sup>2</sup>Zn<sup>2</sup>, and C<sup>2</sup>H<sup>4</sup><sup>2</sup>Zn<sup>2</sup>.

**GASES, DIFFUSION OF.** All gases, even when under existing circumstances they do not enter into chemical combination, yet diffuse themselves through one another and form a uniform mixture, though their specific gravities may be very different and they may be kept externally at perfect rest. If, for example, two bottles be connected by an upright glass tube, 10 inches long and  $\frac{30}{16}$  inch wide, the upper bottle being filled with hydrogen, nitrogen, nitric oxide, or common air, and the lower with the heavier gas, carbonic anhydride, or the upper with hydrogen and the lower with common air, nitrogen, oxygen, or nitric oxide, a portion of the heavier gas will after a few hours be found in the upper bottle, and after two or three days both bottles will contain the two gases in the same proportion (Dalton, Phil. Mag. xxiv. 8). The same result was obtained by Berthollet (Mém. d'Arcueil, ii. 463) with a tube 10 inches long and  $\frac{1}{2}$  of an inch wide, placed in a cellar where no change of temperature could take place to set the gases in motion. When hydrogen was the gas contained in the upper vessel, the two gases were found to be uniformly mixed in 12 days; but when air, oxygen, or nitrogen was contained in the upper vessel and carbonic anhydride in the lower, several weeks elapsed before the mixture became perfectly uniform.

If a cylinder filled with any gas and placed in a horizontal position be made to communicate with the external air by means of a tube bent at right angles, the end of the tube being directed downwards when the gas is lighter, and upwards when it is heavier than the air, the gas will gradually escape from the cylinder, its place being supplied by the air. According to Graham,

Of 100 volumes of gas there disappeared:

Sp. gr.		In 4 hours.	In 10 hours.
1	Hydrogen . . . . .	81.6	94.5
8	Light carburetted hydrogen . . . . .	43.4	62.7
8.5	Ammonia . . . . .	41.4	59.6
14	Olefiant gas . . . . .	34.9	48.3
22	Carbonic anhydride . . . . .	31.6	47.0
32	Sulphurous anhydride . . . . .	27.6	46.0
35.4	Chlorine . . . . .	23.7	39.5

From this it appears that gases escape the more quickly the lighter they are; and their expansive power, or *diffusibility*, varies nearly in the inverse ratio of the square roots of their specific gravities. Thus 47 measures of hydrogen escaped in two hours, and the same volume of carbonic anhydride in 10. Now this proportion of 1 : 5 is nearly that of the square root of 1 (spec. grav. of hydrogen) to the square root of 22 (spec. grav. of carbonic anhydride).

If the cylinder contains a mixture of two gases, the more diffusible of the two will escape in greater proportion into the air, and the less diffusible in smaller proportion, than if each gas were contained in the cylinder alone. Thus, of 50 measures of hydrogen and 50 of olefiant gas, there escape in 10 hours 47.7 measures of the former and 12.5 of the latter: similarly 47 measures of hydrogen and 20 of carbonic anhydride; though in these cases the opening of the bent tube is directed downwards; further, in 4 hours there escape 26.8 vols. of marsh-gas and 12.5 of carbonic anhydride; also 22.8 of marsh-gas and 18.6 of olefiant gas. If two bottles be connected together by a tube placed in a vertical position, the lower bottle being seven times as large as the upper and filled with carbonic anhydride, while the upper one is filled with a mixture of hydrogen and olefiant gas in equal volumes, the upper vessel will, after 10 hours be found to contain, besides carbonic anhydride, a quantity of olefiant gas whose volume is 4 times as great as that of the hydrogen still remaining; the latter has therefore, in spite of its greater levity, diffused itself through the lower vessel with greater rapidity. (Graham, Qu. Jour. of Sc. vi. 74.)

In the same manner also vapours diffuse themselves through one another and through the more permanently elastic fluids.

When different elastic fluids have once diffused themselves uniformly through one another, they never separate again according to their different specific gravities, for however long a time the mixture may be left at rest.

So great indeed is the tendency of gases to diffuse through one another, that this mixture or interdiffusion likewise takes place when the gases communicate with each other through minute pores or apertures of insensible magnitude. Priestley (*Exp. and Obs. on different kinds of air*, iii. 29), in transmitting gases through stone-ware tubes surrounded by burning fuel, observed that the tubes were porous and that the gas escaped outwards into the fire, while at the same time the gases from the fire penetrated into the tube, even though the gas within the tube was in a compressed state. Döbereiner in 1825 made the remarkable observation that hydrogen kept in a cracked glass receiver standing over water escaped by degrees through the crack into the surrounding air, the water under the receiver rising to the height of about  $2\frac{1}{4}$  inches above the outer level. The remaining hydrogen contained

7 per cent. of nitrogen, but no oxygen. If the receiver be filled with oxygen and nitrogen instead of hydrogen, nothing will escape from it. In the same manner hydrogen escapes out of bottles closed even with well-ground stoppers, if the stoppers are not greased. (Döbereiner.)

Graham (*Elements of Chemistry*, 2nd ed. i. 87), in repeating Döbereiner's experiment and varying the circumstances, observed that hydrogen never escapes outwards by the fissure, without a certain portion of air penetrating inwards; in fact, that when hydrogen gas communicates with air through such a chink, the air and hydrogen exhibit a powerful disposition to change places, a particle of air however exchanging with a particle of hydrogen, not of the same, but of 3.83 times its own magnitude. And by extending the observation to different gases, with an instrument admitting of exact measurement of the rate at which the interchange took place, it was found that the diffusion of gases through porous septa is regulated by the same law as when they communicate freely with one another, namely, that *the relative diffusibilities are inversely as the square roots of the densities*.

The instrument with which these observations are made is called a diffusion-tube or diffusimeter. It consists of a glass tube, nearly an inch in diameter, from six to fourteen inches long, open at one end, and having the other end closed by a thin diaphragm of some porous substance. The material originally used was gypsum, which was applied by thrusting into the tube a cylinder of wood of somewhat smaller diameter, so as to occupy the whole of it with the exception of about a fifth of an inch, which space was then filled with gypsum-paste, of the consistence commonly used for taking casts. The plaster sets in a few minutes, and, on withdrawing the wooden cylinder, forms a receiver closed by an immovable plate of stucco, which, though air-tight in the wet state, is permeable to gases when dried by exposure to the air for a day.

When such a diffusion-tube, ten inches long, is filled with hydrogen over mercury, the interchange of air for hydrogen takes place through the minute pores of the stucco with such rapidity, that in three minutes the mercury inside the tube attains a height of three inches above that in the trough, and in twenty minutes the whole of the hydrogen has escaped. In making such an experiment over water, it is necessary to avoid wetting the stucco. With this view, the shorter leg of an inverted siphon is introduced into the diffusion-tube to within an inch of the stucco, and the tube is then sunk in the water-trough, so that the air escapes by the siphon, with the exception of a small quantity, which is noted. The diffusion-tube is then filled up, either entirely or to a certain extent, with the gas to be diffused. (Graham, *Phil. Mag.* 1834, vol. ii.)

In experiments made for the purpose of determining the exact proportion between the gas diffused and the air which replaces it, it is necessary to guard against any inequality of pressure, by placing the diffusion-tube in a jar of water or mercury, and filling the jar with the liquid in proportion as it rises in the tube. Bunsen (*Gasometry*, p. 200) has adapted a lever arrangement to the diffusion-tube, by which the adjustment of the level is greatly facilitated.

A superior material for the porous plate is now found by Graham in the artificially compressed graphite of Mr. Brockedon, of the quality used for making writing pencils. This material is sold in London in small cubic masses about two inches square. A cube may easily be cut into slices of a millimetre or two in thickness by means of a saw of steel spring. By rubbing the surface of the slice, without wetting it, upon a flat sandstone, the thickness may be further reduced to about one-half of a millimetre. A circular disk of this graphite, which is like a wafer in thickness but possesses considerable tenacity, is attached by resinous cement to one end of the glass tube, above described, so as to close it and form a diffusimeter. The tube is filled with hydrogen gas over a mercurial trough, the porosity of the graphite plate being counteracted for the time by covering it tightly with a thin sheet of gutta percha. On afterwards removing the latter, gaseous diffusion immediately takes place through the pores of the graphite. The whole hydrogen leaves the tube in forty minutes or an hour, and is replaced by a much smaller proportion of atmospheric air (about one-fourth), the mercury rising in the tube, if allowed, so as to form a column of several inches in height—a fact which illustrates strikingly the intensity of the force with which the interpenetration of different gases is effected. Native or mineral graphite is of a lamellar structure, and appears to have little or no porosity: it cannot be substituted for the artificial graphite as a diffusion septum. Unglazed earthenware comes next in value to graphite for this purpose.

Dry and sound cork also forms a very good material, but permits the diffusion to go on but very slowly, not being sufficiently porous: so do thin slips of many granular foliated minerals, such as flexible dolomite; charcoal, woods, and dry bladder may also be used for the same purpose.

The following table exhibits the densities of several gases; the square root of the density, or the calculated ratio of the times required for the diffusion of equal volumes, that of air being assumed = 1; the reciprocal of the square root, or the calculated



diffusiveness of the gas; and, lastly, the rates of diffusion, as determined by experiment, the barometric pressure and the temperature being supposed to be the same for all the gases.

*Diffusion of Gases.*

Gas.	Density.	Square root of density.	$\frac{1}{\sqrt{\text{Density}}}$	Velocity of diffusion, air = 1.
Hydrogen . . . .	0.06926	0.2632	3.7794	3.83
Marsh gas . . . .	0.559	0.559	1.3375	1.344
Steam . . . . .	0.6235	0.7896	1.2664	
Carbonic oxide . . . .	0.9678	0.9837	1.0165	1.0149
Nitrogen . . . . .	0.9713	0.9856	1.0147	1.0143
Ethylene . . . . .	0.978	0.9889	1.0112	1.0191
Nitric oxide . . . . .	1.039	1.0196	0.9808	
Oxygen . . . . .	1.1056	1.0515	0.9510	0.9487
Sulphydric acid . . . .	1.1912	1.0914	0.9162	0.95
Nitrous oxide . . . . .	1.527	1.2357	0.8092	0.83
Carbonic anhydride . . .	1.62901	1.2365	0.8087	0.812
Sulphurous " . . . .	2.247	1.4991	0.6671	0.68

The agreement between the observed and calculated rates of diffusion exhibited in this table is very close. It is only, however, when the diaphragm through which the diffusion takes place is very thin, not exceeding  $\frac{1}{8}$  of an inch for stucco, that this closeness of agreement is observed. When thicker diaphragms are used, the gases have to pass through a number of long capillary tubes, the sides of which offer to the passage of a gas a resistance analogous to that of friction, and therefore retard its motion considerably. In fact, the passage of gases through capillary tubes, called "Transpiration," is regulated by laws totally distinct from those of diffusion; the former is a movement of masses, the latter of molecules. (See GASES, TRANSPIRATION OF, p. 820.)

The resistance of a capillary tube to a gas passing through it is proportional to the surface, and consequently increases as the tube or tubes are multiplied in number and diminished in diameter, with the area of discharge preserved constant. The resistance to the passage of a liquid through a capillary was observed by Poiseuille to be nearly as the fourth power of the diameter of the tube. In gases the resistance also rapidly increases, but in what ratio has not been observed. The consequence, however, is certain that, as the diameter of the capillaries may be diminished beyond any assignable limit, so the flow may be retarded indefinitely, and caused at last to become too small to be sensible. We may therefore have a mass of capillaries of which the passages form a large aggregate, but which are individually too small to permit a sensible flow of gas under pressure. A porous solid mass may possess the same reduced penetrability as the congeries of capillary tubes. Indeed the state of porosity described appears to be more or less closely approached by all loosely aggregated mineral masses, such as lime-plaster, stucco, chalk, baked clay, non-crystalline earthy powders, like hydrate of lime or magnesia, compacted by pressure, and in the highest degree perhaps by artificial graphite.

A plate of artificial graphite, although it appears to be practically impenetrable to gas in the mass, is readily penetrated by the agency of the molecular or diffusive movement of gases. This appears on comparing the times required for the passage of equal volumes of different gases under a constant pressure. Of the following three gases, oxygen, hydrogen, and carbonic anhydride, the times required for the passage of an equal volume of each through a capillary glass tube, in similar circumstances as to pressure and temperature, are as follows:

	Time of capillary transpiration.
Oxygen . . . . .	1
Carbonic anhydride . . . . .	0.72
Hydrogen . . . . .	0.44

But through a plate of graphite, of half a millimetre in thickness, the same gases were observed to pass, under a constant pressure of a column of mercury of 100 millimetres in height, in times which are as follows:—

	Time of molecular passage.	Square root of density (oxygen 1).
Oxygen . . . . .	1	1
Hydrogen . . . . .	0.2472	0.2502
Carbonic anhydride . . . .	1.1886	1.1760

It appears then that the times of passage through the graphite plate have no relation to the capillary transpiration times of the same gases. The times in question, however, show a close relation to the square roots of the densities of the respective gases, as is seen in the last Table; and so far they agree with the theoretical *times of diffusion* usually ascribed to the same gases.

The experiments were varied by causing the gases to pass into a Torricellian vacuum, and consequently under the full pressure of the atmosphere. The times of penetration of equal volumes of gases were now—

	Times.	$\sqrt{\text{Density.}}$
Oxygen . . . . .	1 . . . . .	1
Air . . . . .	0.9501 . . . . .	0.9507
Carbonic anhydride . . . . .	1.1860 . . . . .	1.1760
Hydrogen . . . . .	0.2506 . . . . .	0.2502

This penetration of the graphite plate by gases appears to be entirely due to their own proper molecular motion, quite unaided by transpiration. It seems to offer the simplest possible exhibition of the molecular or diffusive movement. This pure result is to be ascribed to the wonderfully fine porosity of the graphite. The interstitial spaces, or channels, appear to be sufficiently small to extinguish transpiration, or the passage of masses, entirely. The graphite becomes a molecular sieve, allowing molecules only to pass through.

With a plate of stucco, the penetration of gases under pressure is very rapid, and the volumes of air and hydrogen passing in equal times are as 1 to 2.891, which is a number for hydrogen intermediate between its transpiration volume 2.04 and diffusion volume 3.8; showing that the passage through stucco is a mixed result.\*

With a plate of biscuit-ware, 2.2 mm. in thickness, the volume of hydrogen rose to 3.754 (air = 1), approaching closely to 3.8, the molecular ratio.

The rate of passage of a gas through graphite appeared also to be closely proportional to the pressure.

Further, hydrogen was found to penetrate through a graphite plate into a vacuum with sensibly the same absolute velocity as it diffused into air, establishing the important fact that the impelling force is the same in both movements. (Graham, Phil. Trans. 1863.)

The passage of a gas through a graphite plate into a vacuum is due entirely to its intestine molecular or diffusive movement, and is to be distinguished from the passage of gas through a minute opening, such as a puncture made by a fine needle in platinum foil. (See GASES, EFFUSION OF.)

*Separation of Gases by Diffusion. Atmolysis.*—A partial separation of mixed gases and vapours of unequal diffusibility can be effected by allowing the mixture to permeate through a graphite plate into a vacuum, as was to be expected from the preceding views. The amount of the separation is in proportion to the pressure, and attains its maximum when the gases pass into a nearly perfect vacuum. When a portion of air confined in a jar is allowed to penetrate into a vacuum through graphite or unglazed earthenware, the nitrogen should pass more rapidly than the oxygen in the proportion of 1.0668 to 1; and the proportion of oxygen be proportionally increased in the air left behind in the jar. The increase in the oxygen actually observed when the air in the jar was reduced from 1 volume

to 0.5	volume, was 0.48 per cent.
0.25	" 0.98 "
0.125	" 1.54 "
0.0625	" 2.02 "

Or, the oxygen increased from 21 to 23.02 per cent. in the last sixteenth part of air left behind in the jar.

The most remarkable effects of separation are produced by means of the *tube-atmolysers*. This is simply a narrow tube of unglazed earthenware, such as a tobacco-pipe stem, two feet in length, which is placed within a shorter tube of glass and secured in its position by corks, so as to appear like a Liebig's condenser. The glass tube is placed in communication with an air-pump, and the annular space between the two tubes is maintained as nearly vacuous as possible. Air or any other mixed gas is then allowed to flow in a stream along the clay tube, and collected as it issues. The gas so atmolysed is of course reduced in volume, much gas penetrating through the pores of the clay tube into the air-pump vacuum; and the more slowly the gas is collected,

\* This may perhaps explain the results obtained by Bunsen who used, in his experiments on diffusion, a stucco diaphragm of considerable thickness, and was led to conclude that the pores of gypsum act upon gases, not as a series of fine openings, but as a series of capillary tubes, and thence to call in question the truth of the law of gaseous diffusion through porous diaphragms deduced from Graham's experiments. (See *Bunsen's Gasometry*, p. 203; also *Graham's Elements*, 2nd ed. li. 624.)

the greater is the proportional loss. In the gas collected, the denser constituent of the mixture is thus concentrated in an arithmetical ratio, while the volume of the gas is reduced in a geometrical ratio. In one experiment, the proportion of oxygen in the air, after traversing the atmolyser, was increased to 24.50 per cent. or 16.7 upon 100 oxygen originally present in the air. With gases differing so much in density and diffusibility as oxygen and hydrogen, the separation is of course much more considerable. The explosive mixture of two volumes of hydrogen and one volume of oxygen, gave oxygen containing only 9.3 per cent. of hydrogen, in which a taper burned without explosion; and with equal volumes of oxygen and hydrogen, the proportion of the latter was easily reduced from 50 to 5 per cent. (Phil. Trans. 1863.)

The atmolytic method may sometimes be advantageously applied to determine whether a certain gas is a mixture or a simple gas; to distinguish, for example, marsh-gas,  $\text{CH}_4$ , from a mixture of equal measures of hydrogen and hydride of ethyl,  $\text{H}^2 + \text{C}^2\text{H}^6$ , each of which would give, when detonated with oxygen, the same proportion of carbonic anhydride and water. But suppose that, after the proportions of carbon and hydrogen have been thus determined, a portion of the mixture is submitted to diffusion, and the residue again analysed; the proportions of carbon and hydrogen will then remain unaltered, if the gas consists of marsh-gas, whereas if it is a mixture, the proportion of hydrogen will be found less than before the diffusion.

The method of diffusion has also been applied to determine whether certain compounds, which, like hydrochlorate of ammonia, yield anomalous vapour-densities (p. 811), are resolved at high temperatures into their components, thus yielding vapours which are no longer chemical compounds, but mixtures. This mode of attacking the question was first proposed by Playfair and Wanklyn (Edinb. Phil. Trans. vol. xxii. Part 3; Chem. Soc. J. xv. 142), and has been carried out as follows by Pebal (Ann. Ch. Pharm. cxxiv. 199). A plug of asbestos, *c*, supporting a few fragments of sal-ammoniac, *d*, is placed within a vertical tube, *c* (fig. 516), drawn out to capillary end, and supported within a wider tube *D*, closed at the top, the whole being surrounded by a charcoal furnace. Both tubes project below the furnace, and are closed at the bottom with corks, through each of which pass two bent tubes, the one for admitting a stream of hydrogen, the other for carrying it off. The heat of the burning charcoal volatilises the hydrochlorate of ammonia in the inner tube above the asbestos plug; so that, if the salt is actually resolved into hydrochloric acid and ammonia, the latter, being the more diffusible of the two, will diffuse downwards through the plug into the hydrogen in the inner tube *c*, and may be demonstrated

Fig. 516.

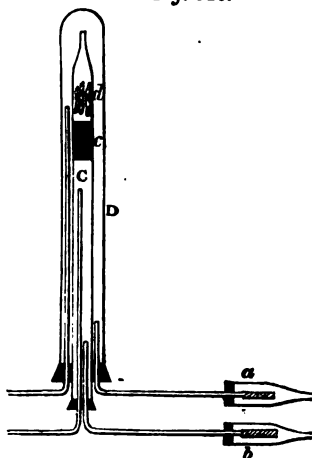
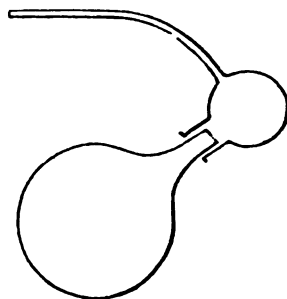


Fig. 517.



by causing the issuing gas to come in contact with a piece of reddened litmus paper, *a*, while the less diffusible hydrochloric acid will remain mixed with the hydrogen in the space *D* between the two tubes; and its presence may be demonstrated by placing a piece of blue litmus paper, *b*, in contact with the gas which issues from that space. Such indeed, is found to be the case; hence Pebal concludes that the sal-ammoniac has been actually resolved by the heat into hydrochloric acid and ammonia.

Messrs. Wanklyn and Robinson (Proc. Roy. Soc. xii. 307) object to this conclusion, that the decomposition of the sal-ammoniac in Pebal's apparatus is probably effected



by the action of the finely-divided silicate forming the porous diaphragm, inasmuch as the acid of that salt, having an indefinite capacity of saturation, may take up the ammonia and set the hydrochloric acid free.\* They therefore discard the use of a porous diaphragm altogether, and allow the vapours to diffuse through a simple aperture, as in Graham's original experiments (p. 811). The apparatus used consists of two glass flasks (*fig. 517*), the necks of which do not fit air-tight: the narrow tube proceeding from the upper one is fused into it. The lower flask is for the reception of the vapour to be operated on; the upper flask is for the atmosphere into which the vapour is to be diffused. The atmosphere of dry air, or other suitable gas, is kept constantly renewed by the transmission of a slow stream of gas, which enters the upper flask by the narrow tube, and passes out by the space between the two necks. The whole apparatus is kept at a temperature above the condensing point of the vapour by means of an air-bath. After the diffusion has gone on for a sufficient length of time, the apparatus is left to cool, and the contents of the lower flask are analysed, by which means it is seen whether diffusion has effected any alteration in the composition of the vapour.

*Sulphuric acid* thus treated is resolved into water and sulphuric anhydride, the vapour of water diffusing more readily than that of the anhydride, and consequently leaving in the lower flask a residue richer in sulphuric anhydride than the acid before diffusion. In one experiment, an acid composed of 95 pts. monohydrated sulphuric acid and 5 water, diffused for an hour at  $520^{\circ}\text{C}$ ., left a residue composed of 60 pts.  $\text{SO}^4\text{H}^2$  and 40  $\text{SO}^4$ . In another experiment, a mixture of 99 pts.  $\text{SO}^4\text{H}^2$  and water, left, after diffusion for a shorter time at  $445^{\circ}\text{C}$ ., a residue containing 75  $\text{SO}^4\text{H}^2$  and 25  $\text{SO}^4$ . In both cases the residues fumed strongly on exposure to the air, and consisted partly of crystals and partly of liquid.—*Pentachloride of Phosphorus* diffused into carbonic anhydride for three quarters of an hour at  $300^{\circ}\text{C}$ . was resolved into free chlorine, which was found in the diffused gases by the reaction with iodide of potassium and starch, and trichloride of phosphorus, which remained in the flask, and when treated with water yielded phosphorous acid, which reduced corrosive sublimate to calomel.

These experiments, as well as that of Pebal, cannot be looked upon as quite decisive of the question which they were intended to solve: for it is possible that the decompositions observed may have been determined, at least in part, by the tendency of the more diffusive vapour to expand into the atmosphere of hydrogen or carbonic anhydride. At all events, the experiments of Deville and Troost already cited (p. 811) show conclusively that, at least in the case of ammonia-salts, the supposed decomposition is not brought about by the action of heat alone.

*Theory of Diffusion.*—The diffusion of gases through one another was regarded by Dalton as a necessary consequence of the self-repulsive property of the particles of gaseous bodies. He considered that each gas expands into the space occupied by the other just as it would into a vacuum; and, in fact, experiment shows that the velocities with which gases diffuse into each other are to one another in the same ratio as the velocities with which they rush into a vacuum through an aperture in a thin plate (p. 818). The ultimate result is certainly in accordance with Dalton's view; still we cannot suppose, as he did, that gases act as absolute vacua to each other; for the actual rate of diffusion of any gas is many thousand times slower than the effusion of the same gas into a vacuum.

But though Dalton's hypothesis cannot be admitted, we must still regard the diffusion of gases as a consequence of that intestine movement of molecules which is now generally recognised as an essential property of the gaseous condition of matter. According to this view, a gas is represented as consisting of solid and perfectly elastic spherical particles or atoms, which move in all directions, and are animated with different degrees of velocity in different gases. Confined in a vessel, the moving particles are constantly impinging against its sides and occasionally against each other, and such collisions take place without any loss of motion, owing to the perfect elasticity of the particles. Now if the containing vessel be porous, like a diffusiometer, then gas is projected through the open channels, by the atomic motion described, and escapes. Simultaneously the external air or gas, whatever it may be, is carried inwards in the same manner, and takes the place of the gas which leaves the vessel. To the same atomic or molecular movement is due the elastic force, with the power to resist compression, possessed by gases. The molecular movement is accelerated by heat and retarded by cold, the tension of the gas being increased in the first instance and diminished in the second. Even when the same gas is present both within and without the vessel, and is therefore in contact with both sides of the porous plate, the

\* In that case, however, the hydrochloric acid gas might be expected to diffuse into the hydrogen more readily than the ammonia, which, though not absolutely retained by the silicic acid at the high temperature of the apparatus, would probably be retarded by it.

movement is sustained without abatement, molecules continuing to enter and leave in equal number, although nothing of the kind is indicated by change of volume or otherwise. If the gases in communication be different, but possess sensibly the same specific gravity and molecular velocity, as nitrogen and carbonic oxide do, an interchange of molecules also takes place without any change in volume. With gases opposed of unequal density and molecular velocity, the amount of penetration ceases of course to be equal in both directions. (See *Graham's Elements*, 2nd. ed. ii. 449; also the article **HEAT** in this dictionary.)

**GASES, EFFUSION OF.** This term is used to denote the passage of a gas into a vacuum through a minute aperture in a thin plate of metal or other substance. Now it can be shown, on mechanical principles, that the velocity with which a gas rushes into a vacuum through such an aperture, is the same as that which a heavy body would acquire in falling from the height of an atmosphere composed of the gas in question, and of uniform density throughout. The height of such an atmosphere will be inversely as the specific gravity of the gas, the atmosphere of hydrogen, for example, being sixteen times higher than that of oxygen. But as the velocity acquired by a falling body varies, not directly as the height, but as the square root of the height, it follows that the rate of flow of different gases into a vacuum must be inversely as the square root of their respective densities. This law has been experimentally verified by Graham (*Phil. Trans.* 1846, p. 573). A jar on the plate of an air-pump was kept vacuum by continued exhaustion, and a measured quantity of air, or any gas, allowed to find its way into the jar through a minute aperture in a thin metallic plate, such as platinum foil, made by a fine steel point, and not more than  $\frac{1}{500}$  of an inch in diameter. With an imperfect exhaustion, the velocity with which the gas flows into the jar increases rapidly till the degree of exhaustion amounts to one third of an atmosphere. Higher degrees of exhaustion do not produce a corresponding increase of velocity, and the difference of an inch in the column of the barometer-gauge scarcely affects the rate at which the gas enters when the vacuum is nearly complete, and the pressure to which the gas is subject approaches that of a whole atmosphere. Through a perforated plate such as that described, 60 cubic inches of dry air entered the vacuum or nearly vacuum receiver in about 1,000 seconds; and in successive experiments, the time of passage did not vary more than one or two seconds.

The velocities of effusion of different gases are given in the following table:—

Gas.	Velocity of Effusion.
Air . . . . .	1
Hydrogen . . . . .	3.613
Marsh-gas . . . . .	1.322
Carbonic oxide . . . . .	1.0123
Nitrogen . . . . .	1.0164
Ethylene . . . . .	1.0128
Oxygen . . . . .	0.950
Nitrous oxide . . . . .	0.834
Carbonic anhydride . . . . .	0.821

For gases which do not differ greatly from the air in specific gravity, these rates correspond very closely with the inverse ratios of the square roots of the densities, and therefore with the rates of diffusion (see Table, p. 814). Nevertheless, the phenomena of diffusion and effusion are essentially different in their nature, the effusive movement affecting masses of a gas, while the diffusive movement affects only molecules; and a gas is usually carried by the former kind of impulse with a velocity many thousand times greater than by the latter.

Mixed gases are effused at the same rate as one gas of the actual density of the mixture; and no separation of the gases occurs, as in diffusion into a vacuum.

**GASES, LIQUEFACTION AND SOLIDIFICATION OF.** See **HEAT**.

**GASES, OSMOSE OF.** This term is applied to the passage of gases through membranous diaphragma such as caoutchouc, bladder, gold-beater's skin, &c. The rate of interchange depends in this case, partly on the relative diffusibilities of the gases, partly on the porosity of the membrane, as well as on the different degrees of adhesion which it exerts upon the different gases, by virtue of which the gas which adheres most powerfully penetrates the diaphragm most easily, and attaining the opposite surfaces, mixes with the other. If the membrane is moist, the result is likewise affected by the different degrees of solubility of the gases in the water or other liquid contained in it.

*Caoutchouc.*—A sheet of caoutchouc tied over the opening of a wide-mouthed bottle full of hydrogen gas, is soon pressed inwards even to bursting. If the bottle be filled with air and placed in an atmosphere of hydrogen, the swelling and bursting take place outward. If a closed bottle of caoutchouc perfectly empty does not distend



when placed in hydrogen gas: but if it contains a small quantity of air, distension takes place. Almost all gases excepting nitrogen exhibit the same relations towards common air as hydrogen does, but in different degrees; they all penetrate caoutchouc with various velocities in order to mix with air. In order to measure these various velocities, a sheet of caoutchouc is tied over the shorter funnel-shaped arm of a siphon-tube; mercury is poured into the other arm, which is made very long, so that a portion of air may remain between the mercury and the caoutchouc; and the shorter arm is introduced under a receiver standing over the mercurial trough and filled with the gas to be examined. The gas penetrates the caoutchouc, mixes with the air, and increases its volume; consequently the mercury in the longer arm is driven upwards, sometimes to the height of 63 inches, and might be driven higher if the caoutchouc could sustain a greater pressure without bursting. By experimenting in this manner on different gases, it is found that the same volume of ammoniacal gas obtains access to the air in 1 minute, as of sulphydric acid in  $2\frac{1}{2}$ , of cyanogen in  $3\frac{1}{2}$ , of carbonic anhydride in  $5\frac{1}{2}$ , of protoxide of nitrogen in  $6\frac{1}{2}$ , of arsenetted hydrogen in  $27\frac{1}{2}$ , of olefiant gas in 28, of hydrogen in  $37\frac{1}{2}$ , of oxygen in 1 hr. 53', and of carbonic oxide in 2 hrs. 40'. Caoutchouc appears from this to absorb gases with different degrees of facility; of carbonic anhydride it absorbs its own volume and swells up in consequence. (Mitchell, J. Roy. Inst. 2, 101.)

*Animal Membranes.*—A moist bladder or moistened gold-beater's skin acts like a sheet of caoutchouc (Mitchell). A moist bladder, two-thirds filled with coal-gas or air, swells when suspended in carbonic anhydride, and finally bursts. In this experiment as much as 40 per cent. of carbonic anhydride sometimes mixes with the coal-gas, while only a very small quantity of the latter escapes into the atmosphere of carbonic anhydride. Hence the water of the moistened bladder absorbs carbonic anhydride and gives it up again on the inner side (Graham, Qu. J. of Sc. vi. 88). A perfectly dry bladder containing air does not distend in carbonic anhydride: a bladder moderately wetted expands to a greater extent than one which is thoroughly soaked; for the thinner the film of water which absorbs the gas, the sooner will the gas reach the opposite surface. If the bladder containing air be moistened with alcohol (which absorbs carbonic anhydride more readily than water does) it will expand in an atmosphere of carbonic anhydride as quickly as if it were moistened by water—but not more so: the alcohol likewise causes it to shrivel and soon destroys its power of transmitting gases. Rubbing the bladder with oil of anise or olive oil (neither of which absorbs carbonic anhydride) prevents the expansion. A wet bladder containing air expands more quickly in sulphydric acid than in carbonic anhydride: after being distended as far as possible in the last-mentioned gas, it will expand still further if placed in an atmosphere of sulphydric acid; whereas if exposed to the air it will regain its original size. A bladder containing air also expands when immersed in water holding carbonic anhydride in solution, but not so quickly as in an atmosphere of the gas. A fish's air-bladder expands under the above-mentioned circumstances more quickly than a urinary bladder: on the contrary, this property is not exhibited by the lining membrane of a fowl's egg or by curried sheepskin: the latter allows air and carbonic anhydride to pass through it with equal facility (Baumgartner, Zeitschrift Ph. Math. 8, 9). These experiments show that gases cannot be preserved in bladders without alteration. If a piece of bladder be tied over the upper and widened end of a glass tube, the tube then filled with water, and its lower end plunged under mercury, the mercury will rise within it to the height of 3 inches, in consequence of the water penetrating the bladder and escaping into the air; but as soon as this height is attained, the pores of the bladder allow air to pass through them and the further rise of the mercury is prevented (Magnus, Pogg. Ann. x. 157). According to Fischer Pogg. Ann. xi. 130) who perhaps made use of a stronger bladder, the mercury may attain the height of 12 inches or even more; it ultimately reaches to the bladder itself, the whole of the water evaporating and leaving nothing but a slimy residue. If a tube, sealed at top and tied over with a piece of bladder at the bottom, be filled with water and exposed to the air, the bladder will be pressed inwards in consequence of the evaporation of the water, and air will enter, not however in bubbles, but dissolved by the water: the air thus introduced collects at the upper end of the tube in the gaseous form, and finally all the water evaporates and the tube becomes filled with air. (Fischer.)

#### GASES, RELATIONS OF, TO PRESSURE AND TEMPERATURE.

The volume of a given quantity of any gas is affected by the pressure and temperature to which it is exposed, according to two general laws, which must be attended to in any comparison of the volumes of different gases. The law of Boyle and Mariotte affirms that the volume of a gas is inversely as the pressure to which it is subjected; this pressure being usually measured in inches or millimetres of mercury (see ELASTICITY, p. 370). The law of Dalton and Gay-Lussac affirms that the volume of a gas



is increased or decreased by  $\frac{1}{573}$  of its bulk at zero, for every centigrade degree of temperature above or below zero (or  $\frac{1}{459}$  of its bulk at Fahrenheit's zero for every Fahrenheit degree). These two laws apply equally to vapours, when at temperatures considerably above their condensing points. Hence two volumes of gas or vapour, at very different pressures and temperatures, may be compared with one another, provided the proper corrections are applied according to the following formulæ:—1°. As  $\frac{h}{h'}$  inches or millimetres are to  $\frac{h}{h'}$  inches or millimetres, so is bulk at  $h'$  to bulk at  $h$ . 2°. As  $273 + t$  is to  $273 + t'$  so is bulk at  $t$  degrees above or below zero C., to bulk at  $t'$  degrees.

Or, if  $V$  and  $V'$  be the volumes of the gas at the respective pressures and temperatures, then

$$V' = V \cdot \frac{h}{h'} \cdot \frac{273 + t'}{273 + t} = V \cdot \frac{h}{h'} \cdot \frac{1 + 0.003663 t'}{1 + 0.003663 t}.$$

To find the volume  $V_0$ , which a given volume,  $V$ , of a gas, at pressure  $h$  (in inches), and temperature  $t^\circ$  C., will occupy, when subjected to a pressure of 30 inches and a temperature of  $0^\circ$  C., we have, in the preceding formula,  $h' = 30$  and  $t' = 0$ , therefore,

$$V_0 = V \cdot \frac{h}{30} \cdot \frac{1}{1 + 0.003663 t}.$$

Regnault has shown that neither of the above laws is absolutely accurate, especially with reference to the condensable gases; but the variations are, for the most part, exceedingly minute, and, except in special experiments, may be altogether disregarded (see HEAT).

**GASES, SPECIFIC GRAVITY OF.** See SPECIFIC GRAVITY.

**GASES, SPECIFIC HEAT OF.** See HEAT.

**GASES, TRANSPIRATION OF.** (Graham, Phil. Trans. 1846, p. 591, and 1849, p. 349; *Elements of Chemistry*, 2nd. ed. i. 82.)—The law of effusion stated on p. 818, is true only under the conditions there specified, viz. that the gas shall pass through a minute aperture in a very thin plate. If the plate be thicker, so that the aperture becomes a tube, very different rates of efflux are observed; and when the capillary tube is considerably elongated, so that its length exceeds its diameter at least 4000 times, the rates of flow of different gases again assume a constant ratio to each other; following, however, a law totally distinct from that of effusion. To examine this kind of motion, called "Capillary Transpiration," the gas was placed over water in a graduated jar, so suspended that the liquid in the jar and in the bath could be easily kept at the same level. The gas was dried by passing it through a tube filled with chloride of calcium, and was then made to pass through a long fine capillary tube, into a receiver standing on the plate of an air-pump; this receiver was sometimes kept vacuum by continued pumping; at other times the state of exhaustion was ascertained at intervals by the pressure-gauge. By this method of observation the following general results were obtained:—

1. The rate of transpiration for the same gas increases, *ceteris paribus*, directly as the pressure; in other words, equal volumes of air, at different densities, require times inversely proportional to the densities. For example, a pint of air of double the density of the atmosphere will pass through the capillary tube in half the time which would be required for a pint of air of the natural density, under an equal propulsive force. This result stamps the process of transpiration with a character quite distinct from that of diffusion or effusion.
2. With tubes of equal diameter, the volume transpired in equal times is inversely as the length of the tube.
3. As the temperature rises, the transpiration of equal volumes becomes slower.
4. The same uniformity in the results was obtained, whether the tubes were of copper or of glass, or whether a porous mass of stucco was employed, provided always that the length of the tubes exceeded their diameter in the ratio above-mentioned.

The rates of transpiration of different gases bear a constant relation to each other, totally independent of their densities, or indeed of any known property of the gases.

A comparison of the numbers in the following table exhibits some very simple relations between the rates of transpiration of certain gases.

1. Equal *weights* of oxygen, nitrogen, air, and carbonic oxide are transpired in equal times.
2. The velocities of transpiration of nitrogen, nitric oxide, and carbonic oxide are equal.
3. The velocities of hydrochloric acid, carbonic anhydride, and nitrous oxide are equal.

*Transpirability of Gases.*

Gases.	Times for transpiration of equal volumes.	Velocities of transpiration.
Oxygen . . . . .	1 0000	1·0000
Air . . . . .	0·9030	1·1074
Nitrogen . . . . .	0·8768	1·141
Nitric oxide . . . . .	0·8764	1·141
Carbonic oxide . . . . .	0·8737	1·145
Nitrous oxide . . . . .	0·7493	1·335
Hydrochloric acid . . . . .	0·7363	1·358
Carbonic anhydride . . . . .	0·7300	1·370
Chlorine . . . . .	0·6664	1·500
Sulphurous anhydride . . . . .	0·6500	1·538
Sulphydic acid . . . . .	0·6195	1·614
Marsh-gas . . . . .	0·5510	1·815
Ammonia . . . . .	0·6115	1·955
Cyanogen . . . . .	0·5060	1·976
Ethylene . . . . .	0·5051	1·980
Hydrogen . . . . .	0·4370	2·288
<b>Vapours.</b>		
Bromine (about) . . . . .	1·0000	1·0000
Sulphuric anhydride . . . . .	1·0000	1·0000
Sulphide of carbon . . . . .	0·6195	1·614
Chloride of methyl . . . . .	0·5475	1·826
Chloride of ethyl . . . . .	0·4988	2·005
Oxide of methyl . . . . .	0·4826	2·072
Hydrocyanic acid . . . . .	0·4600	2·174
Ether . . . . .	0·4400	2·273

4. The velocities of hydrogen and vapour of ether are equal : so likewise are those of sulphydic acid and vapour of sulphide of carbon ; and those of marsh-gas and chloride of ethyl.

5. The velocity of hydrogen is double that of nitrogen, of nitric oxide, and of carbonic oxide.

6. The velocities of chlorine and oxygen are as 3 : 2. The velocities of bromine and of sulphuric anhydride appear to be nearly the same as that of oxygen. No gas appears to be slower than oxygen.

7. The velocities of hydrogen and marsh-gas are as 5 : 4.

8. Ethylene, cyanogen, and ammonia have each nearly double the velocity of oxygen.

The transpiration time of mixtures of the following gases was found to be exactly the mean of the times of the individual gases, viz. oxygen, nitrogen, carbonic oxide, carbonic anhydride, and nitrous oxide ; but the transpiration time of hydrogen and carburetted hydrogen, particularly the former, is greatly increased when these gases are mixed either with one another or with gases of the former class. Thus, the transpiration time of a mixture of equal volumes of oxygen and hydrogen was 0·9008 and not 0·72, the mean time of the two gases. The transpiration time of hydrogen in such a mixture is as high as 0·8016, or its transpiration is then less rapid than that of carbonic anhydride.

The rates of transpiration of the vapours have not been determined with so much accuracy as those of the permanent gases, in consequence of the necessity of experimenting upon them in a state of mixture with some permanent gas.

**GASTERASE.** Syn. with Pepsin ; see the next article.

**GASTRIC JUICE.** (Bidder and Schmidt, *Die Verdauungssäfte und der Stoffwechsel*, Mitau und Leipzig, 1852, pp. 29-97.—Cl. Bernard, *Leçons de physiologie expérimentale*, Paris, 1856, ii. 382.—Huebenet, *Disq. de succo gastrico*, Dorpat, 1850.—E. v. Schröder, *Succi gastrici humani indoles physica et chemica* ; O. v. Grünwaldt, *Succi gastrici humani vis digestiva*, &c., Diss. inaug. Dorpat, 1853.—Lehmann, *Lehrb. der physiolog. Chemie*, Leipzig, 1853, ii. 35-50 ; *Physiological Chemistry*, Cav. Soc. Ed. London, 1851-4, ii. 40 ; iii. 503 ; *Gmelin's Handbuch*. viii. [2] 25.—Pavy, *On the Immunity enjoyed by the Stomach from being digested by its own Secretion during Life*, Proc. Roy. Soc. xii. 386.—C. Schmidt, *Ann. Ch. Pharm.* xcii. 44.)—This fluid, which accumulates in the stomach after the



ingestion of food, is, after being freed by filtration from mucus and fragments of epithelium, perfectly transparent and nearly colourless, having only a slight yellow tint. It has a faint peculiar odour, generally resembling that of the animal from which it is taken, and a scarcely perceptible saline-acid taste. It is slightly heavier than water, neutral or slightly alkaline when taken from the empty stomach, but acid after the ingestion of food; it is not rendered turbid by boiling. At temperatures below  $0^{\circ}\text{C}$ , it solidifies without becoming turbid. It is precipitated by tannin, alcohol, and most metallic salts. If carefully freed from mucus, &c., it may be exposed to the air for months, or even years, without undergoing alteration; and even when a fungous growth has appeared, it still retains its most essential character, viz. its digestive power.

The constituents of the gastric juice are *water, inorganic salts, organic substances, and a free acid*. Its constitution appears to be nearly the same in all vertebrate animals.

The solid constituents do not exceed from 1 to 1.75 per cent. the remaining 98.25 to 99 pts. being water. The solid residue, when incinerated, is found to consist chiefly of *chloride of sodium*, with smaller quantities of *alkaline sulphate, carbonate and phosphate of calcium*, and sometimes *sulphate and chloride of calcium*.

The organic constituents of the gastric juice have been but little examined, in consequence of the extremely small quantities in which they occur. They consist of a substance soluble in water and in absolute alcohol (formerly known as *osmazome*), and a substance soluble in water only. This latter, called *pepsin, chymosin, or gastrase*, is the true digestive principle of the gastric juice. It may be precipitated by treating the juice with alcohol, the greater portion of the other matters then remaining in solution. The precipitate, which contains sulphur and nitrogen, dissolves pretty freely in water, and is thrown down from the aqueous solution by corrosive sublimate, protochloride of tin, basic acetate of lead, and tannic acid, and imperfectly by neutral acetate of lead. The solution is not rendered turbid by boiling, and exhibits strong digestive powers when mixed with hydrochloric or lactic acid; but, like the gastric juice itself, it loses these properties by boiling, by treatment with absolute alcohol, or by neutralisation with alkalis. In an alkaline solution, pepsin soon becomes putrid, and in a neutral solution, it seems to give rise to the formation of fungi; but when rendered acid, it remains unaltered for a long time, exactly like natural gastric juice.

Respecting the nature of the free acid in gastric juice, the opinions of different observers are greatly at variance. Prout (Ann. Phil. new ser. xii. 407), and Bracconot (Ann. Chim. lix. 438), concluded from their own experiments, that the gastric juice contains free hydrochloric acid. Lehmann, on the other hand, found free lactic acid in this secretion, and attributed the free hydrochloric acid given off on evaporating gastric juice in vacuo, to the decomposition of chloride of calcium by the lactic acid. Bernard and Barreswil (J. Pharm. 1845, p. 49) altogether deny the existence of free hydrochloric acid in the gastric juice, on the ground that this liquid in the pure state is rendered turbid by a drop of dilute oxalic acid, whereas an equal quantity of that acid added to a lime-solution containing only  $\frac{3}{1000}$  of free hydrochloric acid produces no precipitate; moreover that starch, after boiling with lactic acid or gastric juice, still gives a blue colour with iodine, whereas it loses this property by boiling with hydrochloric acid. Bernard and Barreswil also find that gastric juice when distilled yields at first a neutral distillate; when concentrated to  $\frac{2}{3}$  of its bulk it yields an acid distillate, in which, however, nitrate of silver produces no precipitate; and it is not till the liquid has been distilled down to a few drops, that the distillate affords any indications of the presence of hydrochloric acid. Von Grönwaldt likewise maintains that human gastric juice contains no free hydrochloric acid, but that the acid reaction which it exhibits when mixed with food, is due to organic acids, chiefly lactic and butyric, either contained in it, or developed from the food.

On the other hand, Bidder and Schmidt have shown, by experiments which scarcely leave room for doubt, that the quantity of chlorine precipitated by nitrate of silver from gastric juice acidulated with nitric acid, is equivalent to a quantity of hydrochloric acid more than sufficient to neutralise all the bases contained in the juice; a portion of this acid must therefore be present in the free state, and the excess, determined as above, was found very nearly equal to the quantity of free acid in the gastric juice, estimated by neutralisation with standard solutions. With regard to the non-appearance of hydrochloric acid in the distillate from gastric juice, excepting in small quantity at the end of the distillation, as observed by Bernard and Barreswil, Schmidt, and likewise Mulder, observe that hydrochloric acid can unite with albuminous substances, forming compounds from which it is not expelled by distillation. (For further details, see *Gmelin's Handbuch*, viii. [1] 29.)

According to Mareet (Chem. Soc. J. xv. 407), the gastric juice of dogs contains



another free acid besides hydrochloric acid. A portion of the gastric juice of a dog, which gave an abundant precipitate with nitrate of silver, being placed upon a dialyser (p. 316), the hydrochloric acid in the liquid gradually passed through the diaphragm into the water below, and after a while the remaining liquid, when freed from albumin by boiling and filtering, gave no precipitate with nitrate of silver, but nevertheless, still exhibited a distinct acid reaction, showing that another acid was present, besides the hydrochloric acid. Acetic acid is said by some authorities to be occasionally present in normal gastric juice.

Of the *abnormal constituents* of the gastric juice, says Lehmann, very little is known. In the normal state, the stomach when empty, is invested with a layer of mucus, which is neutral to vegetable colours. In gastric catarrh, this *mucus*, which differs but little from the secretions of other mucous membranes, accumulates in larger quantities, and when it comes in contact with amylaceous or saccharine food, it enters into abnormal processes of fermentation, viz., acetous, butyrous, and lactous fermentation. The contents of the stomach then contain much more free acid than in normal digestion. The butyrous and lactous fermentations are especially promoted by the presence of fat, giving rise to heart-burn, a sensation of constriction in the throat, and vomiting; and at the same time there is often a revulsory (antiperistaltic) motion of the intestinal tube, which causes a regurgitation of bile into the stomach. *Biliary matters* are almost always present in the stomach, even of recently killed animals; nevertheless, they cannot, strictly speaking, be regarded as normal constituents of the gastric juice, inasmuch as they are never produced from the same sources. In uræmia, or after extirpation of the kidneys, urea is secreted by the gastric glands. *Foreign matters* introduced in solution into the body appear to circulate through the gastric glands; thus Bernard found that when sulphocyanate of potassium and sesquichloride of iron were injected into different veins of the same dog, the red colour of ferric sulphocyanide first appeared in the gastric juice.

The quantity of gastric juice secreted varies greatly at different times of the day; it is least when the stomach is empty, and is promoted by the ingestion of food; even mechanical excitation, such as that produced by swallowing stones or peas, increases the secretion. The effect of different kinds of food in this respect varies considerably. Sugar, aromatic substances, alcohol, and alkalis, immediately excite profuse gastric secretion: animal substances act more slowly, but ultimately give rise to a still larger production of the gastric juice. Psychical causes also increase the secretion, e.g. the sight of food by a fasting animal.

From the experiments of Bidder and Schmidt, made with animals in which gastric fistulæ had been established, it appears that dogs secrete, on the average, in 24 hours for each kilogramme of their weight, 100 grms. of gastric juice, containing 2·883 grammes of solid matter (including lactic acid) and 0·270 grms. hydrochloric acid, the quantity of gastric juice secreted in an hour varying from 24 to 204 grms. per kilogramme of the animal's weight. A sheep secretes per kilogramme in 24 hours 120 grms. of pure gastric juice, containing 1·663 grms. solid constituents, and 0·187 grms. hydrochloric acid.

Schmidt (Ann. Ch. Pharm. xcii. 44) found, by observations on a woman having a gastric fistula, that the quantity of gastric juice secreted, per kilogramme of bodily weight, in 24 hours was 264 grms., containing 1·447 grms. solid matter, and 0·053 grms. hydrochloric acid.

The following table exhibits a comparative view of the composition of the gastric juice obtained from these several sources.

*Composition of Gastric Juice.*

	Man.	Sheep.	Dog.	Ratio.
Water . . . . .	994·404	986·148	971·171	1 : 0·45 : 0·37
Ferment and ammonia .	3·195	4·205	17·507	1 : 0·6 : 2·1
Hydrochloric acid .	0·200	1·557	2·703	1 : 3·5 : 5·1
Chloride of calcium .	0·061	0·114	1·661	1 : 0·9 : 1·04
Chloride of sodium .	1·465	4·368	3·147	1 : 1·3 : 0·9
Chloride and potassium	0·550	1·518	1·073	1 : 1·3 : 0·7
Phosphates of calcium, magnesium and ferri- cum . . . . .	0·125	2·090	2·738	1 : 7·6 : 8·3
	1000·000	1000·000	1000·000	

The acidity of gastric juice ranges, according to Marceet, from 0·085 to 0·303 per

cent. of hydrochloric acid, and varies according to the time, after ingestion of food, at which the secretion is collected. The first quantity removed from the stomach is the most abundant, but the least acid, the secretion gradually becoming smaller in quantity but more acid, and the last quantity exhibiting the highest degree of acidity. This gradual increase of acidity arises partly from the fact that the first quantities of gastric juice secreted are diluted and neutralised by the slightly alkaline mucus contained in the fasting stomach, but more especially, perhaps, from actual increase of the proportion of acid secreted in the latter portions.

The free hydrochloric acid of the gastric juice appears to result from the decomposition of chloride of sodium; this explanation of its origin was first suggested by Prout, who further supposed that the soda separated from it was directed to the liver, and passed off in the bile. But from the experiments of Dr. Bence Jones (*Phil. Trans.* 1849), it appears that, during the secretion of the gastric juice, the acidity of the urine is greatly diminished, and is at its minimum at the time when digestion is at its height; hence it appears probable that, when the chloride of sodium in the blood yields hydrochloric acid to the gastric juice, the soda separated from it at the same time is taken up by an acid which, during fasting, would have been excreted by the urine, but which remains in the circulation while digestion is going on. (Marcet.)

*Physiological action of the Gastric Juice.*—All alimentary substances are permeated and softened by the gastric juice; but its principal action is exerted upon the azotised portions of the food, and on the neutral fats. Most of the non-azotised constituents, gum, sugar, starch, &c., placed in pure gastric juice, at the temperature of the animal body, do not undergo any perceptible alteration; but the neutral fats are resolved by it into glycerin and fatty acids, and are then ready to be transformed into emulsions by the bile, which exerts that action upon fatty acids but not on neutral fats. (Marcet, see DIGESTION, p. 325.)

The albuminous and gelatinous matters are dissolved and converted into new substances, which, although they coincide with the bodies from which they are derived, in composition and in many of their physical properties, nevertheless differ essentially from them in being easily soluble in water, and even in dilute alcohol, and in not forming insoluble compounds with metallic salts. The formation of these compounds, called peptones, depends solely on the action of the gastric juice, and is not attended by the evolution or absorption of any gas, or the production of any secondary substance. Soluble casein is coagulated in the stomach before it undergoes the actual process of digestion.

According to Lehmann, cartilage and gelatinous bodies are converted in the stomach into substances which correspond perfectly in their physical and in most of their chemical characters, with the peptones of the protein-bodies. Marcet has, however, shown that the peptones obtained from gelatinous bodies—or at least one such peptone—possess the power of rotating the plane of polarisation of a ray of light, a character not exhibited by the peptones of the protein substances. Hoppe, in 1859 (*Henne and Meissner's Bericht über die Fortschritte der Anatomie und Physiologie*), observed that gastric juice acts on polarised light, and attributed this action to the gastric secretion itself. Marcet in 1860 made the same observation, but showed further that pure gastric juice, obtained by keeping a dog fasting for thirty hours or longer, then washing out the stomach thoroughly with water, and making the animal swallow siliceous pebbles, has no power of rotating the polarised ray. After exciting the secretion with fragments of bone, however, a gastric fluid was obtained which exerted a slight influence on polarised light, showing a rotation of  $7^{\circ}$  to the left of Soleil's saccharometer; whereas, when the secretion was excited by cartilage, the rotation amounted to  $30^{\circ}$  or  $40^{\circ}$ , also to the left. Gastric juice mixed with cartilage, or with the internal tissue of boiled tripe, and heated in a water-bath to the temperature of the animal body, acquires, after a short time, an optical rotatory power, which may be twice as great as that which it possessed before the commencement of the artificial digestion.

To determine the rotatory power of the polarising peptone, it was separated from the gastric juice, dried, and dissolved in 25 c.c. of water. The solution yielded, for  $1^{\circ}$  of deviation, an average quantity of 0.024 grm. of dry substance. Therefore when gastric juice is examined in the saccharometer, the fluid contains, for every degree of rotation to the left, 0.024 grm. of polarising peptones, or a quantity approximating thereto, in 25 c.c. (Marcet.)

The only two animal tissues which have been observed to yield polarising peptones, are cartilage and the mucous tissue of boiled intestine. No appreciable quantity of polarising substance was obtained from pure coagulated albumin, or coagulated casein, when digested out of the body. (Marcet.)

The constituents of the gastric juice which are mainly essential to the process of digestion are the pepsin and the free acid; but it can scarcely be doubted that every

one of its constituents has a certain share in its action on food. The necessity of a free acid in the digestive process is shown by the fact that the gastric juice, when neutralised by an alkali, completely loses its action on the azotised portions of the food. The acidity of the juice is, however, only one element of its activity: for the digestive power is likewise destroyed by heating the liquid to a temperature near the boiling point, the pepsin, which appears to act like a ferment, being, like other ferments, unable to withstand that temperature.

The neutralisation of the free acid of the gastric juice by an alkali is the cause which prevents the stomach of a living animal from being acted upon and dissolved by its own secretion. During life, the walls of the stomach are very freely permeated by a current of blood, which, in its normal state, is always alkaline, and therefore neutralises the acid in the gastric juice, and protects the stomach from its action. After death, however, the blood becomes stagnant and incapable of supplying the alkali with the same rapidity as a circulating current; consequently, in many cases, especially when death is sudden or violent, and the gastric juice healthy and vigorous, the stomach is found to be dissolved, even to the extent of perforation. This was first noticed by John Hunter (Phil. Trans. 1772), who attributed the immunity of the stomach during life to the vital principle. But Bernard showed that parts of living animals, frogs' legs for example, are digested when introduced through a fistulous opening into a living stomach; and Dr. Pavy has obtained the same result with the extremity of the ear of a living rabbit, clearly showing that it is not vitality which protects the stomach from the action of its own secretion.

The protecting action has also been attributed to the epithelial lining or mucous membrane of the stomach, which, though acted on and dissolved, is constantly renewed, and therefore defends the stomach from injury; but Pavy has shown that a patch of mucous membrane of the size of a crown-piece may be removed from the stomach of a dog, and food afterwards digested, without the stomach showing the least signs of attack.

The only satisfactory explanation of the immunity of the stomach during life is that of Dr. Pavy above mentioned, namely, that the acidity of the gastric secretion is neutralised by the alkalinity of the circulating blood. Even when the circulation through the stomach is arrested during life by ligatures, the mucous membrane is not always attacked, because there is then still a circulation all round the stomach, and from the facility with which the permeation of fluids takes place, a certain amount of counter-active influence is still exerted; but if a dilute non-corrosive acid (phosphoric or citric) is introduced at the same time into the stomach, so as completely to neutralise the alkali of the blood, the gastric juice then exerts its action, and solution and perforation quickly take place.

The digestion of certain living tissues, viz. the frog's legs and the extremity of the rabbit's ear in the experiments above mentioned, probably arose from the supply of blood to those organs not being sufficient to yield the quantity of alkali required to neutralise the acid of the gastric juice.

*Artificial Gastric Juice* is a fluid obtained by treating the glandular tissue of the stomach in a peculiar manner with hydrochloric acid: it possesses, in common with natural gastric juice, the power of converting nitrogenous articles of food into soluble non-coagulable substances. (See Pepsin.)

**GAULTHERIA-OIL**, or *Oil of Wintergreen*, is a volatile oil or essence obtained from the *Gaultheria procumbens* (wintergreen, or Canada tea), a trailing plant of the ericaceous order, which grows abundantly in New Jersey. The oil exists in all parts of the plant, but chiefly in the leaves, whence it is extracted by maceration with alcohol or ether, or by distillation with water. It is colourless when fresh, but on exposure to the air it acquires a red-brown colour, which, indeed, the commercial oil usually exhibits. It has an agreeable aromatic odour, and is used for scenting soaps, &c. It consists of *methyl-salicylic* or *gaultheric acid*,  $\left\{ \begin{array}{l} (C^7H^5O^2) \\ H.CH^3 \end{array} \right\} O^2$  (see SALICYLIC

ETHERS), mixed with a small quantity of *gaultherilene*, a hydrocarbon isomeric with oil of turpentine. When distilled, it begins to boil at  $200^{\circ} C.$ , at which temperature the gaultherilene chiefly passes over, and the boiling point then gradually rises to  $222^{\circ}$ , at which temperature the pure methyl-salicylic acid distils over. On distilling the oil with strong potash- or soda-ley, methylic alcohol, water, and gaultherilene pass over, and salicylate of potassium remains in the retort. (Cahours, Ann. Ch. Phys. [3] x. 327.—Procter, J. Pharm. [3] iii. 276.)

An oil nearly identical in properties with wintergreen oil, and consisting of methyl-salicylic acid, unmixed with gaultherilene, is obtained by distilling with water the bark of the *Betula lenta* (sweet birch, blair birch, cherry birch), a tree growing in North America. This oil does not exist in the bark ready formed, but appears to be produced by the action of a substance resembling emulsin on *gaultherin*, a compound



analogous to the amygdalin of bitter almonds: for, when the dry pulverised bark is exhausted with cold alcohol of 90 per cent., the residue does not yield methyl-salicylic acid by distillation with water; but on evaporating the alcoholic tincture, and treating the residue with water, the odour of wintergreen oil is evolved, and by distillation a liquid is obtained which reddens ferric salts, an indication of the presence of salicylic acid. (Procter, *loc. cit.*)

**GAULTHERIC ACID.** Syn. with METHYL-SALICYLIC ACID.

**GAULTHERILENE.** The hydrocarbon isomeric with oil of turpentine which exists in wintergreen oil. The best mode of isolating it is to distil wintergreen oil with caustic alkali, as above described, wash the heavy oil which settles at the bottom of the watery distillate, first with alkaline, then with pure water, and rectify it over potassium. It is a colourless mobile oil, having an odour like that of pepper. Boils at 160° C. Vapour-density 4.92. It forms a resinous mass with nitric acid, and viscid products with chlorine and bromine. (Cahours.)

**GAY-LUSSITE.** A native carbonate of sodium and calcium,  $2\text{NaCaCO}_3 + 5\text{H}_2\text{O}$ , found at Lagunilla, near Merida, in Columbia, disseminated at the bottom of a small lake in a bed of clay, covering *urao*. The natives call it *clavos* or *nails*. It is also found near Sangerhausen in Thuringia. The crystals are prisms belonging to the monoclinic system, transparent or translucent, with yellowish-white colour, and exhibiting double refraction. Specific gravity 1.92 to 1.99. Hardness 2 to 3. Extremely brittle. Fracture conchoidal, with vitreous lustre on the fractured surface. Streak greyish-white. Decrepitates slightly when heated, and becomes opaque from loss of water. Melts rapidly before the blowpipe to an opaque bead, which has a strong alkaline taste, and when once formed is no longer fusible. The pulverised mineral, before ignition, dissolves sparingly in water without decomposition, forming a solution which reddens turmeric. The anhydrous salt is resolved by water into soluble carbonate of sodium and insoluble carbonate of calcium. (Dana, i. 455; Gm. ii. 216.)

**GEDRITE.** A variety of hornblende, resembling anthophyllite, from Gedré in the Pyrenees. It contains, according to Dufrenoy, 38.81 per cent.  $\text{SiO}_2$ , 9.31  $\text{Al}_2\text{O}_3$ , 45.83  $\text{Fe}_2\text{O}_3$ , 4.13  $\text{Mg}_2\text{O}$ , 0.67  $\text{Ca}_2\text{O}$ , and 2.70  $\text{H}_2\text{O}$ .

**GEHLENITE.** A silicate found mostly at Mount Manzoni, in the Fassa Valley (Tyrol), in isolated or aggregated crystals invested by calcspar. The crystals are short square prisms, sometimes tabular. Cleavage imperfect parallel to the base. Specific gravity 2.9 to 3.067. Hardness 5.5 to 6. Lustre resinous, inclining to vitreous. Colour various shades of green to grey and brown. Fracture uneven—splintery. The powder is easily decomposed by hydrochloric acid, with separation of gelatinous silica. According to Rammelsberg's analysis (*Mineralchemie*, p. 732), the mineral contains—

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{Fe}_2\text{O}$ and $\text{Mn}_2\text{O}$	$\text{Ca}_2\text{O}$	$\text{Mg}_2\text{O}$	$\text{H}_2\text{O}$
29.78	22.02	3.22	1.92	37.90	3.88	1.28 = 100.00

whence may be deduced the formula  $3\text{M}^2\text{O}.\text{M}^4\text{O}^2.2\text{SiO}_2$  or  $\text{M}^2\text{M}^4\text{Si}_2\text{O}^{10}$  (M denoting a monatomic, and  $\text{M}^4$  a sesquiatomic radicle, such as aluminium); and if we write  $m = \frac{2}{3}\text{M}$ , this formula becomes  $\text{M}^2m^2\text{Si}_2\text{O}^{10}$ , which is of the general form  $\text{R}^2\text{Si}_2\text{O}^{10}$ , or  $\text{R}^2\text{SiO}_5 = 3\text{R}'\text{O}.\text{SiO}_2$  (Dana, ii. 256). The term *massive Gehlenite* is applied to a variety of Mellitite (*q. v.*)

**GEIC ACID and GEIN.** See ULMIC ACID and ULMIN.

**GELATIN.** Bone-gelatin. Animal glutin. (Lehmann's *Physiological Chemistry*, i. 39. Gerhardt's *Traité*, iv. 507.)—When bones are digested for some length of time with hydrochloric or nitric acid diluted with 9 pts. water, and the liquid is decanted and replaced by water less and less acid, the whole of the mineral constituents of the bones are dissolved out, leaving the chief organic constituent, bone-cartilage, as a yellowish, transparent, elastic substance, retaining the primitive form of the bone, and becoming exceedingly hard and slightly brittle on drying. This substance, which is also the chief constituent of the serous membranes, the connective tissue, the epidermis, tendons, horn, &c., has been termed ossein, or ostein, by Verdeil and Robin. Ossein, when completely exhausted by dilute acid, contains but a trace of mineral matter; it is washed with distilled water until the wash-waters no longer acquire an acid reaction, then dried, and treated with alcohol and ether. According to Frémy, it always has an acid reaction, which it loses by washing with feebly alkaline water. Boiled with water, ossein is converted into gelatin, without either evolving or absorbing gas; indeed, the composition of the two bodies does not sensibly differ. The presence of an acid greatly facilitates this transformation. Ossein contains 49.2 C, 7.8 H, and 17.9 N (Frémy), with between 0.6 and 0.7 per cent. sulphur. (Verdeil, Schlieper.)

Several kinds of gelatin occur in commerce. The purest, called *ichthyocoll*, or *isinglass*, is extracted from the internal membrane of the swimming-bladder of the sturgeon, a fish very common in Russia. An inferior kind of isinglass is manufactured from fish-bones. *Glue* is a crude product, prepared by boiling down pieces of hide, bones, horn, hoof, cartilage, &c., with water, either at the common atmospheric pressure or under a higher pressure (at 106° or 107° C.). After the concentrated solution has been clarified, it is converted by cooling into a trembling jelly, which is cut into thin slices by means of a wire, and then dried. In this form it is met with in commerce.\* Common glue is far from being pure gelatin: it contains substances soluble in cold water and in alcohol. To purify it, the solution of glue is allowed to gelatinise in cold water, and the jelly is mechanically divided, tied in a cloth, and placed in contact with warm water, which is renewed from time to time. When the whole of the colouring matter has thus been extracted, the jelly is melted in water at a gentle heat, and the insoluble portion is filtered off. The clear solution, mixed with its own volume of alcohol, yields a precipitate of pure gelatin. Gelatin is often prepared by treating bones with dilute hydrochloric acid. The ossein thus obtained is washed and melted in a little water.

**Chemical and physical properties.**—Dry gelatin is a colourless or yellowish substance, transparent in thin plates, elastic, vitreous, hard, and brittle. It has neither taste nor smell, is not affected by the atmosphere, and is neutral to vegetable colours. It is heavier than water, and is insoluble in alcohol and ether. In contact with cold water, gelatin swells and increases about 40 per cent. in weight, becoming translucent, but does not dissolve appreciably. The jelly dissolves in hot water, and the concentrated solution is precipitated by alcohol in the form of a white clotted mass.

When a concentrated solution of gelatin is boiled for some time, it gradually loses the property of gelatinising on cooling, and the liquid on evaporation leaves a deliquescent residue, resembling terebinthin. The solution, however, yields with alcohol a precipitate of the same composition as gelatin.

	Mulder.		Frémy.		v. Goudöver. Gelatin modified by boiling.
	Stag-horn.	Isinglass.	Beef-bones.	Cartilage.	
Carbon . . .	49·4 . .	50·1 . .	50·0 . .	49·81 . .	48·9
Hydrogen . .	6·6 . .	6·6 . .	6·5 . .	7·14 . .	6·5
Nitrogen . .	18·4 . .	18·3 . .	17·5 . .	17·38 . .	17·4
Sulphur . . .					
Oxygen . . .					

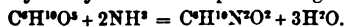
Schlieper found in bone- and ivory-gelatin between 0·12 and 0·14 per cent. of sulphur; and v. Bibra always found very appreciable quantities of sulphur in bone-gelatin. Gelatin precipitated by alcohol gives but a trace of ash. Common glue, however, always contains a large quantity of phosphate of calcium, and, according to Mulder, this substance is an essential constituent of gelatin.

Moist gelatin exposed to the air rapidly putrefies; the liquid at first becomes highly acid, but afterwards gives off a large quantity of ammonia. This property of first becoming acid is characteristic of gelatin.

Submitted to dry distillation, gelatin yields an aqueous distillate charged with carbonate of ammonium, and a thick brown oil containing sulphide, carbonate, and cyanide of ammonium, various volatile alkaloids (aniline, picoline, methylvamine, tritylamine, tetramine, pyridine, lutidine, pyrrol), together with certain neutral oils not yet investigated.

Pure solution of gelatin is not precipitated by *dilute alkalis*. Boiled with concentrated solution of potash, it yields leucine, glycocine, and other products. The same reaction takes place when gelatin is carefully fused with hydrate of potassium.

It is not precipitated or rendered turbid by any acid, except the *tannic acids*. Gelatin is dissolved by concentrated *sulphuric acid* in the cold. The solution, diluted with water and boiled, yields leucine, glycocine (sugar of gelatin), and other products. Gerhardt, by boiling isinglass for several days with dilute sulphuric acid, obtained sulphate of ammonium, and a considerable quantity of a saccharine matter, convertible into alcohol and carbonic acid by fermentation. This reaction supports to a certain extent Hunt's view of the constitution of gelatin. He finds that by adding the elements of ammonia to the formula of starch, and subtracting the elements of water, a formula is obtained agreeing pretty nearly with the composition of gelatin:—



This formula would require 50·70 C; 7·04 H; 19·71 N; and 22·55 O; the nitrogen is much too high.

\* On the manufacture of gelatin for culinary purposes, see *Urc's Dictionary of Arts*, &c. ii. 324; Manufacture of glue, *ibid.* 376.



Gelatin is attacked by hot *nitric acid*, oxalic and saccharic (?) acids being produced, together with a fat and an astringent substance. (Berzelius.)

Lime and phosphate of calcium are much more soluble in a solution of gelatin than in cold water. Chemical compounds of gelatin and phosphate of calcium may be prepared. It is not unlikely that ossein and phosphate of calcium may be in chemical combination in the bones. (Lehmann, *Gmelin's Handbuch*, viii. [2] 557.)

Solution of gelatin is not precipitated by *alum* or *ferric sulphate*; on the addition of alkali in sufficient quantity, a precipitate is formed containing gelatin and a basic sulphate. It is not precipitated by *ferrocyanide of potassium* (this distinguishes gelatin from the protein-compounds), nor by *neutral* or *basic acetate of lead*. It is rendered turbid by the addition of a small quantity of *mercuric chloride*; the precipitate redissolves on shaking, but becomes permanent on the addition of excess of the salt. It is not precipitated by *nitrate of silver* or *chloride of gold*, but reduces them partly to the metallic state. It is precipitated by *platinic chloride*.

*Sulphate of copper* does not precipitate gelatin; the green liquid turns violet on addition of potash, and is not precipitated by ammonia or phosphate of sodium.

By distillation with dilute *sulphuric acid* and *peroxide of manganese* or *acid chromate of potassium*, the same products are obtained with gelatin as with albumin, viz. carbonic acid, formic acid and its homologues up to caproic acid; also prussic acid, valeronitrile, acetic and butyric aldehydes, benzoic acid, hydride of benzoyl, and a heavy oil having the odour of essence of cinnamon.

*Gallotannic acid*, and other kinds of tannic acid, form compounds with gelatin. The precipitate, from concentrated solutions, is obtained in clotted flakes, or as a soft, elastic, imputrescible mass. The precipitate is insoluble in water, alcohol, and ether, but soluble in a warm solution of potash. It becomes hard and brittle on drying. 100 pts. gelatin dried at 130° C. yield, with gallotannic acid, between 134 and 135.6 pts. product. The composition of the precipitate does not appear to be constant. This reaction is so delicate that a solution containing 0.0002 pts. gelatin is rendered turbid by an infusion of gall-nuts (p. 763).

When a current of gaseous *chlorine* is passed through a solution of gelatin, a white pellicle forms round each bubble of gas, and the whole of the gelatin is finally precipitated in flexible, elastic, nacreous, gelatinous, transparent flakes or filaments (Thénard, Bouillon-Lagrange). The precipitate is tasteless, slightly acid, imputrescible, insoluble in water and in alcohol, and soluble in alkalis. On exposure to the air it exhales an odour of chlorine. A similar product is obtained with gelatin which has been boiled for some time with water. No similar products are obtained by substituting bromine or iodine for chlorine.

*Sources and physiological relations.* Bone-gelatin is obtained from the following tissues by boiling them for a longer or shorter time with water: from the cartilages of bone (after ossification), from tendons, the skin, calves' feet, harts' horns, isinglass, the scales of fish, and from the permanent cartilages, when they become ossified by disease (see CHONDRIN, i. 930). The conversion of these animal parts into gelatin proceeds without any evolution or absorption of gas. Indeed, a comparison of the analyses of pure gelatin with those of the tissues yielding it shows that there is no chemical difference between the two, or that at most they differ only by a few molecules of water. Hence it appears that, in the formation of gelatin, the material of the tissues merely undergoes a re-arrangement of its atoms, or that at most it only assimilates water, just as starch does when converted into glucose by prolonged boiling. The formation of gelatin from the gelatinous tissues is greatly facilitated by the presence of acids. Schlieper found that the ossein of fossil bones, the organic substance of which had been preserved, had been converted into a gelatinous substance or into true gelatin. That of diseased bones does not appear to differ from normal ossein. In the bones of certain waterfowl, and in the ribs of certain fishes, Frémy found, instead of ossein, an organic body isomeric with that substance, but incapable of being converted into gelatin by boiling. The fibrous tissue of embryos does not yield gelatin by boiling with water. It contains an intercellular substance yielding a gelatinous substance and albumin. (Scherer.)

According to J. Müller (*Pogg. Ann.* xxxviii. 313), the cornea contains, not gelatin but a substance resembling chondrin. In cases of leucocythemia, Scherer found gelatin in the blood. The filtered serum of the pus from a femoral abscess was found to contain gelatin (*Gmelin's Handbuch*, viii. [2] 527). Beef contains 1.9 per cent. tendinous tissue capable of being converted into gelatin by boiling with water. (Berzelius.)

Liebig has remarked that gelatin has the property of inducing saccharification.

Gelatin, and tissues yielding gelatin, are converted in the stomach into substances which correspond perfectly in most of their physical and chemical properties with the peptones of albuminoids, but are distinguished by the power of turning the plane of



polarisation of a luminous ray to the left (p. 824). Ready-formed gelatin is more easily metamorphosed than connective tissue, and the latter far more readily than tendons or cartilage.

Gelatin and gelatinous tissue belong to the most digestible substances. According to Blondlot, when a dog was fed with 100 grms. gelatin from calves' feet, very little remained undissolved in the stomach after three quarters of an hour; and in one hour the stomach was empty. The same observation was made with ichthyocoll. Gelatinous tissue, previously boiled, readily undergoes the same change. Pieces of leather were not in the slightest degree acted upon by five days' digestion in a dog's stomach. (*Gmelin's Handbuch*, viii. [2] 616.)

According to Frerichs, digested gelatin loses on cooling the properties of gelatinising and of being precipitated by chlorine, but still gives the characteristic precipitate with tannic acid. The same effect is not produced by artificially digesting gelatin with a dilute acid.

The nutritive qualities of gelatin have been much disputed. Liebig ascribes little if any nutritive qualities to it, but his experiments do not appear to be quite conclusive. In jellies, &c., it does not perhaps add much to the highly nutritive properties of the substances for which it usually serves as a vehicle. C. E. L.

**GELATIN, VEGETABLE.** See GLUTEN.

**GELIDIUM CORNEUM.** See the next article.

**GELOSE.** (Payen, *Compt. rend.* xlix. 521; *Précis de Chimie Industrielle*, 4<sup>me</sup> éd. ii. 727.)—A gelatinous principle which forms the essential constituent of a vegetable substance called Chinese moss (*mousse de Chine*), first imported into France from China in 1856. This substance, which is found in commerce in small bundles of long and very fine threads, is said to be obtained from several lichens growing on trees in the south of China, and the southern islands of the Philippine Archipelago. It is quite destitute of organised structure, and contains only 0·0607 per cent. of matter soluble in cold water, and a still smaller quantity, viz. 0·007 per cent. soluble in alcohol. It swells up in cold water, and dissolves almost wholly in boiling water, leaving only a small quantity (2 or 3 per cent.) of azotised corpuscles. The solution on cooling coagulates into a colourless translucent jelly, containing a quantity of water equal to about 500 times the weight of the original substance.

This jelly, when dried, yields *gelose*, a substance insoluble in cold water, alcohol, ether, weak solutions of potash, soda, or ammonia, dilute acids, and ammoniacal solution of copper. Acetic acid of 8° Bm. dissolves it. It is soluble also in a very small quantity of strong sulphuric or hydrochloric acid, acquiring a brown colour, and gradually forming a brown coagulum, which may be washed without alteration in hot or cold water, or in caustic alkaline solutions.

Gelose contains 42·770 per cent. carbon, 5·775 hydrogen, and 51·455 oxygen. No definite compound has yet been formed of it, so that its atomic weight and rational formula must for the present remain undetermined; but it belongs to that class of proximate principles which contain a larger proportion of oxygen than is required to form water with the hydrogen.

The species of lichen which yield the commercial article are not exactly known. Payen has examined several lichens with the view of obtaining it, but has only found slight traces. On the contrary, he has obtained it in abundance from certain algae, viz. the Java sea-weed (*Gelidium corneum*), and the *Plocaria lichenoides*, a sea-weed from the Mauritius; in small quantity also from several European algae. From Java sea-weed it is extracted by treating the plant in the cold successively with dilute hydrochloric acid of 0·02, or dilute acetic acid, water, and weak ammonia; washing it thoroughly to remove earthy and alkaline salts (including 53 per cent. of carbonate of calcium), and extraneous organic matter; exhausting the residue, which contains 58 per cent. of glucose, with boiling water as above; and drying the jelly which forms on cooling.

Gelose yields ten times as much jelly as an equal weight of isinglass, and may, therefore, perhaps be economically used in place of that substance. It is true that it contains no nitrogen; but as gelatin is said to serve rather as a vehicle for nutritious matter, than as a directly nutritious substance, it is possible that gelose may be found applicable to the same purpose.

**GEMS, ARTIFICIAL.** See *Ure's Dictionary of Arts*, &c. ii. 328.

**GENTIAN.** *Gentiana lutea*.—The root of this plant, which is abundant in Switzerland, the Tyrol, and the Auvergne, is cylindrical, knotted, of yellowish-brown colour, disagreeable odour, and strong bitter taste. The aqueous infusion is much used as a tonic. The root contains gentianic acid, a peculiar bitter called gentian-bitter, uncrystallisable sugar, gum, a volatile oil, a green oily matter, pectic acid, yellow colouring matter and cellulose.

Gentian-bitter may be separated from the aqueous infusion of the root by animal charcoal, and extracted therefrom by hot alcohol. It is yellow, uncrystallisable, and reduces an alkaline cupric solution.

The liquid from which the bitter has been extracted by animal charcoal retains in solution a large quantity of uncrystallisable sugar, and a substance which imparts to it a strong green iridescence or fluorescence. (H. Ludwig, Arch. Pharm. [2] cxi. 132; Jahresh. 1861, p. 753.)

**GENTIANIC ACID.**  $C^{14}H^{10}O^4$ . *Gentianin, Gentisic acid, Gentisin.*—An organic acid existing in the root of gentian (*Gentiana lutea*), discovered by Henry and Caventou (J. Pharm. vii. 173), more fully examined by Baumert (Ann. Ch. Pharm. lxii. 106). It is extracted by treating the powdered root with cold water, to remove the bitter principle; then pressing, drying, and exhausting it with strong alcohol; distilling off the greater part of the alcohol; and treating the brown, resinous, very bitter residue with water, which separates light-brown flakes containing gentianic acid, a resin similar to caoutchouc, a fatty substance, and a bitter principle. They are treated with ether to remove the fat, and then dissolved in alcohol, which leaves on evaporation a crystalline mass, still bitter, and mixed with resin. By repeated crystallisation from alcohol, the gentianic acid is obtained in needles, quite tasteless, and having a light-yellow colour; 10 kilogrammes of the dried root yield only 3 or 4 grms. of pure gentianic acid. (Baumert.)

Gentianic acid crystallises in slender needles, which require 36.30 pts. of water at  $16^{\circ}$  C. to dissolve them. It is more soluble in ether, and still more in boiling alcohol. The solutions are neutral to vegetable colours. It is also very soluble in alkalis, a small quantity sufficing to impart a golden tint to an alkaline liquid. It contains, according to Baumert's analysis, 65.06 per cent. C, 4.12 H, and 30.82 O, agreeing nearly with the formula  $C^{14}H^{10}O^4$ .

Gentianic acid is unalterable in the air, and may be heated to  $200^{\circ}$  C. without decomposing. Between  $300^{\circ}$  and  $340^{\circ}$  it sublimes partially in yellow needles, the greater part, however, becoming carbonised and emitting a peculiar odour. It is not attacked by hydrochloric, acetic, sulphurous or dilute sulphuric acid; strong sulphuric acid dissolves it with yellow colour. Nitric acid of specific gravity 1.43, free from nitrous acid, dissolves it, forming a green solution from which water throws down a green powder, consisting of dinitrogentianic acid,  $C^{14}H^8(NO^2)^2O^4 + H^2O$ . This acid, in contact with alkalis, assumes a fine cherry colour, even the ammonia in the air sufficing to produce it in a certain degree. When gentianic acid is added by small portions to fuming nitric acid, the violent action being each time allowed to subside before a fresh portion is added, a solution is obtained from which water precipitates a yellow crystalline substance, probably consisting of trinitrogentianic acid,  $C^{14}H^7(NO^2)^3O^4$ .

Chlorine passed into an alcoholic solution of gentianic acid throws down light-yellow flocks containing chlorine.

Gentianic acid decomposes alkaline carbonates. The gentianates of the *alkali-metals* are soluble and crystallise in needles, but do not appear to be of constant composition. The *barium-salt* forms an orange-coloured flocculent precipitate, containing  $C^{14}H^8Ba^2O^4 + H^2O$ . The *lead-salt* is also an orange-coloured precipitate, obtained by adding gentianic acid mixed with ammonia to neutral acetate of lead: it contains  $C^{14}H^8Pb^2O^4$ .  $PbHO$ .

Gentianic acid forms green precipitates with cupric salts, brown with ferric salts, and reduces salts of silver.

**GENTIANIN.** Syn. with GENTIANIC ACID.

**GEOCERAIN.** A waxy body isomeric with geoceric acid.

**GEOCERIC ACID.**— $C^{29}H^{44}O^4$ ? (L. Brückner, J. pr. Chem. lvii. 1; Jahresh. 1852, p. 647).—A waxy acid similar to and perhaps identical with cerotic acid, obtained, together with other waxy and resinous substances, from some peculiar kinds of earthy lignite found at Gerstewitz, near Weissenfels.

A yellowish-brown variety of the lignite exhausted with ether yielded by evaporation a yellowish-brown residue, consisting: 1. Of a resinous substance, leucopetrin,  $C^{26}H^{42}O^3$ , insoluble in alcohol of 80 per cent., but slightly soluble in boiling absolute alcohol, whence it crystallises in tufted groups of needles, melting above  $100^{\circ}$  C.—2. Of waxy and resinous substances, soluble in boiling alcohol of 80 per cent. One of these latter, precipitated from the concentrated and cooled alcoholic solution by alcoholic acetate of lead, separated from the lead precipitate by strong acetic acid, and recrystallised from alcohol, formed small needles. Its solution yielded a dirty green precipitate with cupric acetate; its ammoniacal solution gave off all the ammonia on evaporation. Brückner assigns to the substance which unites with the

bases in these salts the formula  $C^{24}H^{21}O^7$ , and calls it georetic acid.—3. The filtrate from the lead precipitate contained two resins, one of which separated by slow evaporation in the pulverulent form, and exhibited the composition  $C^{22}H^{20}O^2$ , and the other separated after further evaporation as a soft, tough, brown, transparent mass.

The same variety of the lignite subjected to dry distillation gave off a large quantity of illuminating gas and white vapours, which at first condensed to an oily liquid, afterwards to a buttery mass, the solution of which in boiling alcohol of 80 per cent. yielded on cooling a combustible crystalline substance, geocerinone,  $C^{110}H^{110}O^2$ , or  $C^{55}H^{55}O$ , the acetone of geocerlic acid, which, when purified by recrystallisation, exhibited microscopic six-sided plates, melted at  $50^{\circ}C$ ., was not altered by aqueous potash, but was converted by chromic acid in the nascent state into a waxy acid. The alcoholic liquid from which the geocerinone had separated retained an oil in solution.

A dark brown variety of the lignite, freed from georetic acid and other resins by exhaustion with cold alcohol of 80 per cent. yielded, on subsequent boiling with the same alcohol, the following substances: 1. The hot-filtered alcoholic liquid deposited on slight cooling, a pulverulent substance, geomycin,  $C^{24}H^{24}O^4$ , or  $C^{12}H^{12}O^2$ , which, however, was obtained in greater quantity when the resin, after exhaustion with cold alcohol of 80 per cent., was boiled with absolute alcohol. After several recrystallisations, it formed white pulverulent masses of microscopic capillary crystals, melting between  $80^{\circ}$  and  $83^{\circ}C$ .—2. The still hot alcoholic liquid, filtered from the geomycin, heated to the boiling point, and mixed with a hot alcoholic solution of acetate of lead, deposited the lead-salt of geocerlic acid, which was extracted therefrom by strong acetic acid, and purified by recrystallisation from alcohol. This acid may also be obtained by saponifying the waxy bodies contained in the alcoholic decoction of the lignite with potash, decomposing the soap with chloride of barium, and the purified barium-salt with acetic acid. It dissolves readily in hot alcohol, and separates almost completely on cooling in the form of a gelatinous mass. It melts at  $82^{\circ}C$ . Brückner expresses its composition by the formula  $C^{24}H^{24}O^4$ , or  $C^{12}H^{12}O^2$ , and observes that it closely resembles cerotic acid,  $C^{27}H^{54}O^2$ .—3. The liquid filtered from the precipitate of geocerate of lead contained in solution a neutral wax, geoceraïn, isomeric with geocerlic acid, which separated from the hot-filtered liquid, on cooling, in the gelatinous form, and, when purified, melted at  $80^{\circ}C$ .

**GEOCERINONE.**  $C^{55}H^{55}O$ .—The acetone of geocerlic acid, obtained by dry distillation of either the yellow-brown or the dark brown variety of the lignite of Weissenfels.

**GEOCRONITE.** (Dana, ii. 85; Gm. iv. 176.)—A native sulphantimonite of lead,  $5Pb^2S.Sb^2S^3$ , or  $\left\{ \begin{smallmatrix} Pb^2 \\ Sb^2 \end{smallmatrix} \right\} S^4$ , from the silver mines of Sala in Sweden; also found in Galicia, at Meredo in Spain, where it forms nodules in galena, and in the Valley di Castello, near Pietro Santo, in Tuscany. Usually massive, but sometimes in crystals belonging to the dimetric system; also granular or earthy. Specific gravity 6.4 to 6.6. Hardness = 2 to 3. Lustre metallic. Colour and streak from light lead-grey to greyish blue. Fracture uneven. Crumbles easily and soils the fingers. Fuses readily before the blowpipe, giving off fumes of antimony and sulphur, and colouring the charcoal yellow. A variety called *Kilbrickenite*, from Kilbricken, County Clare, Ireland, contains 6 at. lead to 1 at. antimony;  $6Pb^2S.Sb^2S^3$  or  $\left\{ \begin{smallmatrix} Pb^{12} \\ (Sb^2)^1 \end{smallmatrix} \right\} S^4$ .

	Geocronite.			Kilbrickenite.
	From Sala. Svanberg.	From Meredo. Sauvage.	From Tuscany. Kerndt.	Apjohn.
Sulphur . . . . .	16.26	16.90	17.32	16.36
Antimony . . . . .	9.58	16.00	9.69	14.39
Arsenic . . . . .	4.69	. . .	4.72	. . .
Lead . . . . .	65.45	64.89	66.55	68.87
Copper . . . . .	1.51	1.60	1.15	. . .
Iron and Zinc . . . . .	0.53	. . .	Iron 1.72	0.38
	98.02	99.39	101.15	100.00

**GEODE.** A rounded nodule of stone containing a cavity usually lined with crystals: geodes frequently consist of lignite, chalcedony, &c.

**GEOLOGY, CHEMISTRY OF.** Since the severance of geological science, properly so-called, from the speculative systems of cosmogony, with which it was associated up to the commencement of the present century, its development has been materially aided by the application of the knowledge acquired in other departments of research, to the critical examination of geological phenomena, and to the elucidation of



the various problems suggested by them, as to the mode in which rocks and strata have been formed or altered from their original conditions. It being no longer regarded as the object of geology to discover how the earth originated, but merely to ascertain the history of its existence and changes, it is evident that the records of that history must be read in accordance with those laws of nature which are known to obtain in the phenomena and changes taking place at the present time. An eminent geologist, in referring to the relation between geology and other physical sciences, has remarked that, as an historian should be at once profoundly acquainted with all branches of knowledge by which any insight into human affairs, or into the moral and intellectual nature of man, can be obtained, so "it would be no less desirable that a geologist should be well versed in chemistry, natural philosophy, mineralogy, zoology, comparative anatomy, botany; in short, in every science relating to organic and inorganic nature." (*Lyell's Principles*, p. 2.)

This necessity, now fully acknowledged by all geologists, has been complied with to a less extent in the case of chemistry than in any other. And yet it is from chemistry alone that data can be obtained which will admit of correct conclusions being formed as to many geological phenomena, such, for instance, as the formation and alteration of rocks and strata, or of the individual minerals of which they are constituted. Prior to the latter part of last century, chemistry was not in a position to furnish the necessary data for the interpretation of geological facts, and the opinions of geologists with regard to the formation and alteration of rocks and strata conformed to one or other of two extreme views, according to which, on the one hand, everything was supposed to have been produced by fire, while on the other hand, everything was supposed to have been produced by water. These two opposite doctrines were equally adopted, without any inquiry being made as to how far the nature of particular rocks or minerals might be consistent with the opinion that they had been produced by the agency of fire or of water. Thus granite and all similar crystalline rocks were very generally regarded as having acquired their present condition by the crystallisation of melted masses; but in granite it is always found that quartz, the least fusible of its three constituent minerals, appears to have been the last to crystallise, while felspar, the most fusible of them, appears to have crystallised first, the crystals of felspar being imbedded in those of mica and quartz. In syenite and other crystalline quartzose rocks, as well as in granite, the quartz is found to be, as it were, the matrix in which the crystals of the other more fusible minerals are imbedded: hence it would appear that the constituent minerals of these rocks were not crystallised in such an order of succession as would be indicated by their relative degrees of fusibility, and as might be expected if they were of igneous origin.

Granite dykes and veins, not more than an inch or two thick, and sometimes as thin as paper, are frequently met with traversing and extending into other rocks, which must have been very intensely heated if these veins were injected in a melted state; but generally speaking the strata in which such veins are found do not present any indications of having been, at any period, intensely or at all heated, nor is there at the lines of contact between the granite veins and the surrounding rock any indication of the action of heat.

These facts, and many others of a similar nature, are quite irreconcilable with the opinion that granite has in all cases been formed by igneous action; and if they do not prove that it has not been so formed, they at least open a wide field of inquiry as to the conditions under which granite has been produced.

The various kinds of porphyritic lava furnish another instance in which the characters of the minerals they contain are inconsistent with the opinion that these rocks were formed, as they now exist, from melted masses. These rocks are undoubtedly of volcanic origin, but the important fact with regard to them is, that they are all of very remote origin, far anterior to the historic period. Generally speaking, the lava of more recent periods is either amorphous, or if it be of crystalline texture, it rarely presents imbedded crystalline minerals of any size or symmetry, so as to have a porphyritic character. It is only in the most ancient products of volcanoes that such crystals of wernerite, garnet, leucite, and vesuvian are met with. A variety of circumstances connected with the relation these minerals bear to others with which they are associated in these rocks, all tend to the conclusion that they have been formed subsequently to the solidification of the lava, and not at all under the influence of heat.

The existence of hydrated minerals, such as zeolites, in some rocks may also be regarded as evidence that those rocks have not been formed by igneous action, or that they have undergone some considerable alterations by other means subsequent to their formation. Thus, for instance, no zeolites are found in lava, but in many kinds of basalt they are very abundant.

Iron-pyrites is a very frequent constituent of most crystalline rocks, but this mineral is decomposed by a red heat. Its occurrence likewise in almost every variety of sedimentary rock is clearly indicative of its formation without the agency of heat,

and lends probability to the same mode of formation in crystalline rocks. It is therefore necessary to abstain from regarding crystalline minerals, occurring even in volcanic rocks, as being products of fusion, or from regarding their occurrence in such rocks as evidence of their formation in that way; and it is still more necessary to abstain from concluding that rocks whose geognostic relations indicate an eruptive origin were originally in the same condition that they exhibit at the present time.

The class of rocks comprised under the general term of metamorphic rocks, have always furnished wide scope for speculation as to the mode in which they have acquired their present condition. These rocks, presenting evident signs of stratification, fossil remains, and sometimes all the features of sedimentary strata, also possess a structure more or less crystalline, and sometimes a general character so closely resembling that of massive crystalline rocks, as to be distinguishable from them only by retaining faint signs of stratification which reveal their sedimentary origin. Hence it has been impossible to overlook the fact that the present condition of these rocks has been brought about by the alteration of sedimentary strata. Very remarkable theories of metamorphism have at various times been propounded, in which fire and water, pressure, electricity, and magnetism have been made to perform strangely incoherent and anomalous functions; but it is only quite lately that any attempts have been made to trace, as it were, the various stages of metamorphism in rocks, and by ascertaining what mineralogical and chemical differences accompany these various degrees of alteration, to obtain a basis on which to found some general view with regard to the metamorphism of rocks, that shall be consistent with observed facts, and with recognised principles of chemistry and physics.

Among the facts which have contributed to afford evidence of the extent to which chemical action is concerned in the formation and alteration of rocks, the phenomena of pseudomorphism and petrification have been the most important. Pseudomorphs are minerals presenting definite crystal-forms which do not belong to the substances of which those minerals now consist, but to other substances which have either wholly disappeared, or of which some fragments still remain. Pseudomorphs, though presenting an outward crystal-form, are not really crystals, but merely aggregates of the substances which have been produced simultaneously with the destruction of those whose outward crystal-form they present. In like manner petrified or fossil organic remains are abundantly met with, consisting of a variety of substances, such as carbonate of calcium, the sulphates of barium, calcium, and strontium, fluoride of calcium, quartz, opal, talc, sesquioxide of iron, the carbonates of zinc, lead, and iron, black oxide of manganese, phosphate of iron, iron and copper pyrites, the sulphides of lead, zinc, copper, and mercury, metallic copper, chlorite, &c. Here the organic substance, or the material of the bony or shelly structures, has been removed, while in their place, and with their form, some one or other of the above-named substances have been substituted.

The alterations recognisable, to a greater or less extent, in many minerals are perfectly analogous to those presented by pseudomorphs and petrifications, and this is equally true whether it be an isolated crystal of a mineral that is altered, or whether the alteration has taken place throughout an extensive mass of rock consisting of minute crystals of that mineral or merely amorphous masses of it. In the latter case, the indications of the change which has taken place cannot be traced as in a large well-defined crystal, but the clue to the real nature of that change may be obtained from the study of the more apparent instance.

Strictly speaking, it may be impossible to say whether any particular mineral is really in a normal condition of integrity, or whether it has not undergone some degree of alteration. The analysis of minerals almost invariably indicates the presence of minute quantities of substances not belonging to their chemical constitution. These substances, regarded as foreign or accidental, are often deducted in calculating the chemical formulæ. Thus for instance, andalusite is reasonably considered to be anhydrous silicate of alumina, but all analyses of this mineral indicate the presence of potash, lime, magnesia, the oxides of iron and manganese, and water. If these substances are merely accidental admixtures, that variety of andalusite which contains the smallest amount of them will be nearest to its normal condition.

The alteration of minerals is an extremely slow process. The material changes progress so gradually as to be chemically recognisable only after the lapse of long periods. Andalusite, for example, is known to undergo conversion into mica, in which change part of the alumina is removed, while potash, magnesia, and ferric oxide are introduced in its place; hence it may be inferred that this mineral, as usually met with, is already in a state of incipient alteration. Andalusite also undergoes conversion into steatite, in which change the whole of the alumina is abstracted, and magnesia substituted in its place.

This example will suffice to show the importance, in a geological point of view, of the



minute quantities of substances present in minerals. These acquire significance when compared with the constituents of the pseudomorphs resulting from the alteration of minerals in which such adventitious substances are found. They then no longer appear accidental, but indicative of the transition of one mineral into others; they place clearly before us the progressive nature of those changes, whose ultimate results are recognisable more obviously in pseudomorphs, and show that those constituents of a mineral, which in a minimum proportion are regarded as accidental, may ultimately in a maximum proportion become essential.

There can be no doubt that the chemical analysis of minerals would acquire a much higher value if its object were not merely to establish chemical formulae, but also to elucidate the formation of minerals. The fact that one mineral may appear with the outward form of another totally distinct mineral has been sufficiently well established by mineralogists, and it remains for chemists to trace the processes by which the alteration of the one into the other may take place. Time being so essential an element in the processes by which these changes are effected, it is not to be expected that they can be experimentally studied; so that the only course is to ascertain by analysis the increase of the non-essential, and the decrease of the essential constituents of mineral, until a point is reached at which the one takes the place of the other.

These processes may be considered to consist either in the direct conversion of one mineral into another, or in the production of a series of gradational changes, furnishing minerals more distinct from the original ones, and more resembling the final product of the alteration. Thus, magnetic iron ore may be directly converted into ferric oxide, while in the case of more complex minerals, such as silicates containing several bases, there would be a long series of transitions, as in the alteration of cordierite, terminating in the formation of mica, the minerals fahlunite, chlorophyllite, bonsdorffite, esmarkite, oolite, weissite, praseolite, gigantolite and pinite are pseudomorphous minerals, representing the different stages of alteration, and hence they cannot be regarded as individual mineral species.

With a knowledge of the substances removed and introduced at any stage of such alterations, it may be possible to arrive at some conclusions as to the means by which those alterations have been effected, which could not otherwise be accessible. It would not perhaps be possible to effect the conversion of augite, olivine, or hornblende into serpentine experimentally; but when serpentine is found with the forms of those minerals, that fact may be taken as evidence that such a conversion has taken place.

If it be ascertained that a crystalline mineral may undergo conversion into another mineral, which, as a pseudomorph, presents the crystal-form of the original mineral, it may be safely inferred that the former mineral, in an amorphous condition, might undergo the same alteration. In such a case, however, the indication afforded by the crystalline form of the original mineral, as to the origin of the product of alteration, would be wanting. So, besides the positive evidence afforded by pseudomorphs, they also furnish the probability that similar alterations may have taken place in amorphous masses without their being recognisable. Thus, serpentine may have been, in some instances, formed by the alteration of amorphous rocks possessing the composition of augite, olivine, or hornblende; and, on the other hand, minerals which, like mica, have an individual crystalline form, may in some instances, where they occur with their proper form, have been formed by the alteration of amorphous masses.

In seeking to arrive at a knowledge of the means by which these gradually progressive alterations of minerals and rocks are effected, it is necessary to take into account a variety of influences which, though infinitesimal in themselves, within ordinary periods of observation, are nevertheless capable of producing, by long continuance, effects which appear at first sight disproportionate. Chief among these are the actions exercised by water, and by the substances it contains in solution, upon the minerals and rocks with which it comes in contact.

The water, falling as rain, penetrates rocks, and yields up the oxygen and carbonic acid it contains to substances capable of combining with them. It also extracts from the rocks it traverses such substances as are soluble in water alone, or by the aid of carbonic acid. In some cases water, penetrating to great depths, meets with subterranean sources of carbonic acid, by absorbing which its solvent capability is greatly increased. The chief constituents of all rocks, excepting limestone, dolomite, and gypsum, are silicates, containing alumina, magnesia, the oxides of iron and manganese, and alkalis. The action of water upon these compounds consists, not merely in solution, but also in the decomposition of the silicates by the aid of the carbonic acid it contains. The porosity of rocks, which such a penetration of water presupposes, is a very general character even of the most compact rocks. In basalt, for instance, small ochrey spots are often found in the interior, consisting of hydrated oxide of iron, and in some cases carbonate of calcium is minutely disseminated throughout the entire



mass of a compact basalt. Both these substances must be regarded as resulting from the decomposition of the silicates of iron and calcium existing in the basalt, by carbonic acid and oxygen conveyed into it by water.

Silicate of calcium is readily decomposed both by solutions of carbonic acid and alkaline carbonates, but silicate of magnesium is not decomposed by either. This very different behaviour of the silicates of earths otherwise so analogous, is of considerable geological importance, and serves at once to account for the well-known facts of the ready disintegration of rocks containing silicate of calcium, and the extreme durability of those containing silicate of magnesium. It also explains why steatite and talc, consisting in their purest forms only of silicate of magnesium, are among the most unalterable minerals, and why they so often appear as the final products of the alteration of minerals.

The decomposition of silicate of calcium by alkaline carbonates, and the frequent presence of the latter in the water percolating through rocks, afford a clue to the conversion of wernerite into mica, a change consisting merely in the substitution of potash for lime. In like manner, most of the alterations indicated by pseudomorphs may be traced to reactions between constituents of the original minerals and alkaline carbonates, acid carbonate of calcium, or carbonic acid, substances which are very commonly present in water.

Of the substances present in water, some, such as earthy carbonates, are no doubt derived, by direct solution, from rocks with which it comes in contact; but there are others, such as the alkaline carbonates, which do not exist in any rocks. Such substances can only be supposed to originate from the decomposition of minerals contained in the rocks; and when water containing earthy or metallic carbonates issues from rocks consisting wholly of silicates, it is probable that those carbonates are also derived from the minerals contained in the rocks, by decomposition.

The uniformity in the characters of the water of mineral springs shows that such processes of alteration are continuous and of considerable magnitude. As illustrations of the effects of such decomposition of silicates in rocks, the conversion of felspar into kaolin and clay may be mentioned as one of the most important. The decomposition of ferruginous silicates by the action of carbonic acid and oxygen is also one of the chief causes of the alteration and disintegration of rocks. The effects thus produced by water and the substances contained in it are not always of a destructive nature. Water containing alkaline silicates or silicate of aluminium is capable of giving rise to the production of silicate of calcium by reacting with sulphate of calcium; silicate of magnesium may be formed by the reaction of such water with magnesian salts, and ferrous silicates may be formed by the reduction of ferric silicates by the carbonaceous substances in the sedimentary rocks. This change appears indeed to be an essential feature of the metamorphosis of rocks. The brown-coloured argillaceous deposits of rivers contain iron solely in the state of ferric oxide and ferric silicate, while the slate rocks, which have undoubtedly originated from such deposits, contain chiefly ferrous silicates. In this series of changes it will be seen that, as in the phenomena of vegetation and animal life, the atmosphere is also concerned. The oxidation of ferrous and manganous compounds which is so prominent a feature of the disintegration of rocks, is attended with an abstraction of oxygen from the atmosphere; while in the reduction of ferric and manganic compounds, under the influence of organic substances, the oxygen thus abstracted, is again restored to the atmosphere, either in the state of carbonic acid or in its original condition, after having passed through an intermediate phase of plant-nutrition: while the carbon, which has been the means of this restoration of the oxygen by the ferric oxide of iron, again assumes a condition in which it may eventually repeat the same function.

So, throughout all the various phenomena of mineral alteration, it is possible to trace for almost every process of decomposition, a compensatory reproductive process by which the substances concerned in the former change are reproduced. The changes of this latter kind are, however, less directly recognisable, since the chief seat of rock formation, in its earlier stage of sedimentary deposit, is to a great extent inaccessible to observation. In the bed of the ocean the materials continually carried down in solution, and mechanically suspended in the water of rivers, contribute, partly under the influence of chemical action, to the formation of new strata. Notwithstanding the large quantities of carbonate and sulphate of calcium thus carried into the sea, there is every reason for the opinion that the composition of sea-water is as little subject to change as the composition of the atmosphere; for as this is maintained constant by the balanced and mutually supporting functions of animal and vegetable life, so the composition of sea-water is maintained constant by the consumption of the carbonate of calcium carried into it by rivers, in the formation of the shells of fish and by coral animals, which appear to be the chief agents of the production of limestone strata. It is in the sea also that a great number of changes are effected in sedimentary deposits,



resulting in the conversion of such deposits as those situated beneath and in the neighbourhood of Amsterdam, into masses of slate, and probably of gneiss and similar rocks. There, the materials furnished by the mechanical and chemical disintegration of rocks still situated above water, are now undergoing the same changes as those which at some earlier period gave rise to the production of the former rocks, whose subaqueous formation is indicated by the fossil remains embedded in them.

This cyclical character of geological phenomena is very generally recognisable, not only in regard to the destruction and formation of rocks, but also in all the processes of mineral alteration; and though there are certain minerals which very generally appear as final products of alteration, such as mica, steatite, talc, quartz, &c., it is probable that they should be regarded in this light but relatively, and that, in reality, they only represent particular stages of wider cycles of alteration which are still unrecognised.

B. H. P.

**GEOMYRICIN.**  
**GEORETIC ACID.** } See GEORETIC ACID.

**GERMINATION OF PLANTS.** To enable a seed to germinate, the following conditions are necessary:—

1. *Full maturity of the Seed itself.*—Only the ripe seed contains the necessary quantity of those constituents on which the nutrition of the young plant depends, before it has attained sufficient development to enable it to derive its nutriment from the air and from the soil. Some seeds contain peculiar compounds, not found in other parts of the plant; and, in all, certain proximate principles are developed in peculiar abundance, especially the azotised bodies, albumin, legumin, and gluten, with a corresponding quantity of earthy phosphates.

2. *A certain temperature.*—The temperature required for the germination of most seeds is from 10° to 30° C. (50° to 86° F.); some, however, will germinate at temperatures as low as 4° C. (40° F.) The vitality or germinating power is absolutely destroyed by exposure to too great a degree of heat, but not by cold. Seeds can withstand much greater extremes of temperature than the other parts of plants, their vitality not being destroyed by a cold of -50° C. (-58° F.), or by a heat of 62° C. (153° F.) in an atmosphere of steam, or of 75° C. (167° F.) in a dry atmosphere.

It is commonly stated that seeds will not germinate when exposed to light. This does not appear, however, to be strictly true. Germination takes place certainly more quickly in the dark; but Saussure found that mustard seeds when kept in moist atmospheres—some under a transparent, and others under an opaque shade—both germinated with equal rapidity; hence he concluded that the retarding action usually ascribed to light is really due to heat, which desiccates the seeds.

3. The presence of *water*, which dissolves certain constituents of the seed, and thus enables them to act upon the insoluble matters; whereas in the absence of moisture all the constituents of the seed remain in the solid state, and no chemical action can take place. Too much water, however, impedes germination, by completely removing the soluble matters.

All seeds contain a certain quantity of water within their own substance; but they do not lose their germinating power by being dried in vacuo over sulphuric acid—that is to say, they are still capable of germinating when placed in contact with water. Some seeds lose their vitality when dried by heat; others do not, provided the heat applied is only sufficient to expel the water. The seeds of *Phaseolus vulgaris*, *Portulaca oleracea*, *Campanula rapunculoides*, and *Papaver somniferum*, lose their vitality when dried in the shade at 35° C.; but those of barley, maize, lentils, hemp, garden cress, mustard, and lettuce, retain it under the same circumstances. Wheat, rye, vetches and cabbage seeds, retain it even at 70° C. When a seed has once germinated, and is then dried, it remains dormant, after being moistened, for a longer time than those which have not germinated.

4. The presence of *oxygen*. Seeds will not germinate in a vacuum, in hydrogen, nitrogen, carbonic anhydride, or carbonic oxide, in water deprived of air by boiling, or covered with a layer of oil, or when buried too deeply in the soil. They often begin to germinate under these circumstances, but quickly decay. Germination takes place with peculiar facility in presence of water containing a little chlorine, probably because the chlorine decomposes the water, and sets oxygen free. In the absence of light, or at low temperatures, when this decomposition does not take place, the presence of chlorine is rather hurtful than otherwise. Strong chlorine-water completely destroys the vitality of seeds.

Gladstone found that the germination of onions was accelerated by the addition of 8 per cent. of marsh gas to the air (Jahresb. d. Chem. iii. 552). According to Violette (Compt. rend. xxxviii. 905), wood-charcoal is peculiarly favourable to germination. Potato-germs immersed in charcoal powder in a close vessel, and kept

in a dark place through the winter, germinated freely; while similar germs immersed in peat-ash, wood-ash, powdered gypsum, slaked lime or dry sand, were found in a state of putrefaction. According to A. Vogel, jun. (Ann. Ch. Pharm. lxxviii. 196), germination is completely arrested by arsenic and its compounds, by oxide and carbonate of copper, by mercurous chromate, and by Prussian blue; and retarded by fluor spar, mercuric oxide, *antimonium crudum*, stannic oxide, carbonate of magnesium, ammonio-magnesian phosphate, and smalt; whereas several other substances which exert a poisonous or a deleterious action on the animal organism—viz. mercury (metallic, or in the form of tin-amalgam), cinnabar, calomel, litharge, phosphate of lead, chromate of lead, *vitrum antimonii*, and carbonate of barium—do not interfere with the germination of seeds. The experiments were made with cress-seed. The statement that arsenic-compounds completely arrest germination is at variance with the well-known practice of steeping wheat-grain in a solution of arsenious acid for the purpose of destroying fungi.

The germination of seeds is accompanied by the following phenomena:—

1. The seed absorbs water, swells up and softens. The harder the seed-coatings, the more slowly does the absorption of water, and consequently the germination, take place. According to Stein (J. pr. Chem. lxxiii. 42), different seeds absorb in 24 to 48 hours (by which time the maximum of water appears to be taken up) from 22 to 116 times their weight of water.

2. The seed pushes forth its germ to a slight extent, and gives off a little carbonic anhydride; these changes taking place whether oxygen is present or not.

3. It absorbs a certain quantity of oxygen. According to Saussure, bean and lettuce seeds absorb 1 per cent., barley and purselain from 0.1 to 0.2 per cent. of their weight of oxygen.

4. It gives off carbonic anhydride, the volume of which, according to Scheele and Saussure, is equal to that of the oxygen absorbed. According to Bousisingault, on the other hand, the volume of carbonic anhydride evolved is sometimes less than that of the oxygen absorbed, part of the carbon being oxidised, only to carbonic oxide.

5. The oxidation-process just mentioned gives rise to a development of heat, sometimes, as in the malting of barley, sufficient to induce spontaneous combustion.

6. The chemical changes which take place in the seed during germination are attended with loss of weight. 100 pts. by weight of barley, which had lost 12 pts. by drying, yielded 80 pts. of dry malt. Of the 8 pts. thus lost, four were removed in the softening of the seed by water, the remaining four in the actual germination. (Thomson, Thoms. Ann. x. 388; Hermstädt, Schw. J. 33, 249.)

7. The insoluble non-azotised matters in the seed—viz. the starch and fat—are converted into soluble compounds, and are thereby enabled to pass from the parts of the seed in which they were developed into the various cells and organs of the growing plant. In this process, the azotised matters of the seed appear to play the same part that bodies of similar constitution discharge in alcoholic fermentation: that is to say, they absorb oxygen, and, being thus thrown into a disturbed state, they communicate the disturbance to the non-azotised bodies with which they are in contact; the result of which is that the starch of the seed is converted into sugar and gum, and the fats appear to be resolved into fatty acids and glycerin. The heat evolved in germination is, perhaps, due in great part to the fixation of water by which these transformations are accompanied. (Röschleder, *Gmelin's Handbuch*, viii. [1] 147; Pelouze et Frémy, *Traité*, vi. 313.)

W. Knop (Rép. Chim. app. 1862, p. 249) has observed that the presence of free alkali is unfavourable to the germination and healthy development of plants. It is well known that when healthy seeds are sown in pure quartz-sand or pounded glass, and watered with saline solutions, the plants, though appearing green and vigorous at first, often turn yellow after a while, and ultimately perish. This etiolation is sometimes attributed to the absence of iron salts, which are necessary to the development of chlorophyll; it may, indeed, sometimes be remedied by watering the plants with weak iron solutions. But from Knop's experiments it appears that the chief cause of the etiolation is the development of alkali in the act of germination. Plants growing in solutions of nitre decompose the nitric acid, and set the alkali free. The juices expressed from the roots and green leaves of healthy plants are always slightly acid. Knop finds that plants growing under the circumstances above-mentioned may be rendered green and healthy by addition of a small quantity of free acid to the solutions with which they are watered, and attributes the beneficial effect of iron-salts rather to the acid which they contain than to the iron. The well-known fact that seeds germinate for the most part better in spring than in the middle of summer, is attributed by Knop to the more rapid production of ammonia in summer, by the decomposition of albuminous matters in the soil; this ammonia being absorbed by the roots, the sap becomes alkaline, and the leaves turn yellow and fade.



**GERSDORFFITE.** Syn. with NICKEL-GLANCE.

**GEYSERITE.** Syn. with OPAL.

**GIBBSITE.**  $\text{Al}^3\text{H}^3\text{O}^3 = \text{Al}^3\text{O}^3, 3\text{H}^3\text{O}^3$ .—Native trihydrate of aluminium, called also *Felsobanyite*, and in the crystallised form, *Hydrargyllite*. It is found at Gumuchdag in Asia Minor, at Richmond in Massachusetts, and other localities in the United States, usually in stalactitic masses, with smooth surface, and indistinctly fibrous structure, exhibiting a faint lustre on the surface. Specific gravity 2.3 to 2.4. Hardness 3 to 3.75. The crystallised variety (*hydrargyllite*), is found near Slatoust in the Ural, in small hexagonal prisms, with replaced lateral edges, and very distinct basal cleavage; specific gravity 2.287; pearly lustre on the base. Both varieties are translucent, tough, exhale a strong argillaceous odour when breathed upon, give off water when heated, and exhibit before the blowpipe the usual characters of aluminium-compounds. They yield by analysis 63.5 to 65.6 per cent. alumina, and 33.8 to 34.7 water (calculation, 65.6  $\text{Al}^3\text{O}^3$ , and 34.4  $\text{H}^3\text{O}^3$ ).

Hermann found in the gibbsite of Massachusetts a large but variable quantity of phosphoric acid, whereas other analysts have found little or none; the discrepancy arises, most probably, from the occasional admixture of phosphate of aluminium with the hydrate. On this account, Rammelsberg (*Mineralchemie*, p. 145) applies the name *hydrargyllite* to the hydrate of aluminium, and *gibbsite* to the phosphate.

**GIESECKITE.** A pseudomorph of NEPHELINE (*q. v.*)

**GIGANTOLITE.** A hydrous dichroïte (p. 320) found in a gneissoid granite at Tammela, in Finland. Crystalline form the same as that of dichroïte, with basal cleavage usually perfect, and sometimes micaceous. Hardness = 3.5, but on the cleavage-surface, 2. Specific gravity 2.862–2.878. Colour greenish to dark steel-grey. Lustre vitreous and waxy, approaching to submetallic. Melts before the blowpipe, with intumescence, to a greenish slag. Contains, according to Wachtmeister's analysis: 46.27 per cent.  $\text{SiO}^2$ , 25.10  $\text{Al}^3\text{O}^3$ , 14.04  $\text{Fe}^3\text{O}^3$ , 2.70  $\text{K}^2\text{O}$ , 3.80  $\text{Mg}^2\text{O}$ , 6.00  $\text{H}^3\text{O}$ , with 0.89  $\text{Mn}^2\text{O}$ , 1.20  $\text{Na}^2\text{O}$ , and a trace of fluorine. If the greater part of the iron be regarded as protoxide ( $\text{Fe}^3\text{O}^3$  2.83,  $\text{Fe}^2\text{O}$  11.61), the composition of the mineral will be that of dichroïte + 4 at. water. (Dana, ii. 216.)

**GILBERTITE.** A variety of BIAXIAL MICA.

**GILDING.** See GOLD.

**GILLINGITE.** Syn. with HISINGERITE.

**GIN.** An ardent spirit prepared from corn, and generally flavoured with juniper-berries. (See *Ure's Dictionary of Arts, &c.*, ii. 337.)

**GINGER.** There are two varieties of this root, the black or grey, and the white. Both are prepared from the root-stocks of *Zingiber off.*, about a year old; the former by scalding them in hot water and drying in a stove, the latter by peeling and drying them in sunshine without previous immersion in hot water. White ginger contains, according to Bucholz, volatile oil, 1.56 per cent.; extract soluble in alcohol, 0.05; extract insoluble in alcohol, 10.50; gum, 12.50; starch, 19.75; mucilage, 8.36; woody fibre, 8.00; matters insoluble in potash, 26.00; water, 11.90; resin, 3.60. (Pelouze et Frémy, *Traité*, vi. 370.)

**GINSENG.** A root found in China, and said by the Chinese to possess extraordinary medicinal virtues. It appears, however, to be identical with the *Panax quinquefolium*, a plant which is likewise found in North America, and does not possess any such qualities. From the root of the American ginseng, Garrigues has obtained a neutral substance called PANACULONE (*q. v.*)

**GIORBERTITE.** Syn. with MAGNESITE.

**GIRASOL.** A variety of OPAL.

**GISMONDIN.** Syn. with ABRAZITE.

**GITHAGIN.** See SAPONIN.

**GLAIADIN** or **GLIADIN.** See GLUTEN.

**GLAIRIN.** See BAREGIN (i. 500).

**GLANCE.** A name applied to minerals having a metallic or pseudometallic lustre; *e. g.*, glance-coal, iron-glance, antimony-glance, &c.

**GLASERITE.** Native sulphate of potassium. (See SULPHATES.)

**GLASS.** (Gm. iii. 377.)—Glass is a mixture of silicate of potassium or sodium, or of both, with one or more silicates insoluble in water, as silicate of barium, strontium, calcium, magnesium, aluminium, manganese, iron, or lead. Pure silicate of potassium or sodium, or a mixture of the two, even with a sufficient quantity of silica to form a

very infusible glass, would still be attacked by water and acids. Silicate of calcium is likewise acted on by acids; but a mixture of it with silicate of potassium or sodium resists their action. Such mixtures of silicate of sodium or potassium with silicate of calcium, &c., are more fusible than the simple salts, and require a smaller amount of silica to render them capable of resisting the action of water and of acids. They contain between 2 and 3 atoms of silica to 1 atom of base, and still less when alumina is also present. The glass is less fusible, and offers greater resistance to the action of water and of acids, the larger the proportion of silica and alumina it contains; and, on the contrary, it is more easily fused, and attacked by water and acids, the more the potash, soda, baryta, lime, magnesia, or oxide of lead predominates; an excess of the last-mentioned oxide renders it particularly fusible, of a high specific gravity, soft, easily scratched, and corroded by acids. According to Baudrimont and Pelouze (*J. Chim. méd.* ix. 277), the lustre and refractive power of glass increase with the atomic weight of the bases contained in it; thus these qualities are possessed in the highest degree by lead-glass, next by baryta, next by potash, and least of all by soda-glass.

The following substances yield the ingredients necessary for the formation of glass:

*Silica*: Ground quartz or flint, or quartz-sand, which is sometimes treated with hydrochloric acid to free it from adhering sesquioxide of iron.—*Potash*: Pearlash and wood-ashes (this likewise yields lime and sesquioxide of iron).—*Soda*: Carbonate of sodium; sulphate of sodium with charcoal (which decomposes the sulphuric acid); native and artificially prepared soda (which at the same time yields lime); common salt, by which the potash-glass—produced by using carbonate of potassium—is decomposed into soda-glass and chloride of potassium.—*Baryta*: Heavy spar mixed with charcoal, or carbonate of barium; rarely employed. According to Baudrimont and Pelouze, 1 at. of heavy spar with 3 at. of sulphate of sodium and 4 at. of charcoal yields a peculiarly brilliant, fusible, and easily worked glass, resembling flint-glass.—A mixture of 70 pts. (1 at.) of carbonate of potassium, 54 pts. (1 at.) of carbonate of sodium, 99 pts. (1 at.) of carbonate of barium, and 224 pts. (7 at.) of silica yields a very transparent glass, which scratches window glass (Döbereiner, *Pogg. Ann.* xv. 243).—*Strontia*: Sulphate of strontium with charcoal, or carbonate of strontium. 70 pts. (1 at.) of carbonate of potassium, 54 pts. (1 at.) of carbonate of sodium, 47 pts. (1 at.) of carbonate of strontium, and 224 pts. (7 at.) of silica yield a remarkably beautiful glass, specifically heavier, more refractive, and much more fusible than crown glass (Döbereiner).—*Lime*: Lime after being burned and slaked, in powder; chalk marl (which also yields alumina), wood-ashes; the same exhausted with water; ball-soda.—*Oxide of lead*: Litharge, minium, white lead, or 1 at. of galena with 3 at. of sulphate of sodium, whereby 4 at. of sulphurous anhydride are evolved.—*Alumina*: Quartz-sand containing clay, marl, felspar, basalt, pumice-stone, and other minerals containing silicate of aluminium and an alkali-metal: they must not however be added in too large quantity, because the presence of too much alumina produces in the glass a tendency to crystallise. The mass of fused glass dissolves alumina from the pots.

*Oxidising agents*, as nitre, arsenious acid, and peroxide of manganese, are added in the preparation of white glass, partly to oxidise the carbon contained in the wood-ashes or ball-soda,—which would render the glass brown,—partly to convert the protoxide of iron into sesquioxide, inasmuch as a quantity of iron which in the state of protoxide would give the glass a dark bottle-green colour, will, if converted into sesquioxide, impart to it a light yellow tint of much less intensity. If too much sesquioxide of manganese is added, so that the carbon and the protoxide of iron cannot reduce it all to the state of protoxide, which dissolves in the glass without producing any colour, a portion is taken up in the state of sesquioxide, which stains the glass red; an excess of arsenious acid imparts to the glass a white turbidity.

*Substances causing turbidity*.—Bone-ash produces a milkiness in the glass, forming what is called Bone-glass; stannic oxide renders lead-glass opaque, and converts it into Enamel.

*Colouring agents*.—Blood-red: cuprous oxide. Carmine-red: purple of Cassius. Violet-red: peroxide of manganese. Blue: oxide of cobalt, oxide of copper. Green: the same substances, together with sesquioxide of iron; sesquioxide of chromium. Yellow: oxide of antimony, sesquioxide of iron. Yellow with a greenish cast: sesquioxide of uranium.—Aventurin glass contains, according to Wöhler (*Pogg. Ann.* lviii. 286), fine octohedral segments of metallic copper. (See *AVENTURIN GLASS*, i. 476.)

The above ingredients, powdered and mixed in the proper proportions, constitute the Glass-frit. This is in most cases first exposed in the *frit-oven* to a gentle heat, which expels water and part of the carbonic acid, and diminishes the subsequent swelling or frothing up of the mass. It is then put into large crucibles called glass-pots, made of very refractory clay, six of which are commonly arranged on ledges in a circular or oblong furnace, and exposed to a continually increasing heat for twelve or

more hours, till the mass becomes free from bubbles, grains of quartz, and streaks. Chloride of potassium, chloride of sodium, sulphate of potassium, and sulphate of sodium float on the surface in the form of a thin fluid stratum, which is skimmed off: the scum is called Glass-gall, or Sandivir. The glass is then formed into the required shapes, and afterwards cooled from a red heat, as slowly as possible, in the *annealing furnace*.

**Bottle-glass.**—Specific gravity about 2·732; very infusible on account of the small proportion of potash and soda, and the large quantity of alumina which it contains.—*a*. From *Souvigny*. Prepared from quartz-sand, marl, elutriated wood-ashes, and a portion of common salt. The phosphoric acid present in the glass arises from the phosphate of calcium in the wood-ashes (Berthier). Its composition is nearly  $3(\text{Ca}^2\text{O} \cdot 3\text{SiO}^2) + \text{Al}^2\text{O}^3 \cdot \text{SiO}^2$ .—*b*. From St. Etienne. In the preparation of this glass heavy spar is employed (Berthier).—*c*. From Epinac. Prepared by simply fusing together two different kinds of sand, one of which contains 61·7 per cent. of carbonate of calcium, 35·6 of carbonate of barium, and 1·2 of clay, the other (a mixture of quartz-sand and felspar), 6 per cent. of potash, 2 of sesquioxide of iron, 0·7 of sesquioxide of manganese, 11 of alumina, and 80 of silica (Berthier).—*d*. From *Sèvres*. This glass is with difficulty reduced to a white mass, which is neither crystalline nor fibrous in its texture (Dumas).—*e*. Of unknown origin; easily converted into fibro-crystalline sort of Reaumur's porcelain. (Dumas.)

**Pale green Glass used for Medical Bottles and Chemical Apparatus.**—Hard; bears changes of temperature better than white glass. *a*, *b*, *c*, *d*, are four French varieties analysed by Berthier.

	Bottle glass.					Glass for medical bottles.			
	<i>a</i> .	<i>b</i> .	<i>c</i> .	<i>d</i> .	<i>e</i> .	<i>a</i> .	<i>b</i> .	<i>c</i> .	<i>d</i> .
K <sup>2</sup> O . . . . .	3·1	3·2	3·2	5·48	6·1	10·6	10·5	8·0	16·4
Na <sup>2</sup> O . . . . .								3·0	
Ba <sup>2</sup> O . . . . .		0·9							
Ca <sup>2</sup> O . . . . .	22·3	20·7	18·0	29·22	28·1	10·0	16·2	13·0	15·6
Mg <sup>2</sup> O . . . . .		0·6	7·0					0·6	2·2
Mn <sup>2</sup> O . . . . .	1·2		0·4			0·3	1·2		
Fe <sup>2</sup> O <sup>3</sup> . . . . .	4·0	3·8	4·4	5·74	6·2	1·5	2·5	1·6	0·7
Al <sup>2</sup> O <sup>3</sup> . . . . .	8·0	10·4	6·8	6·01	14·0	3·0	4·5	3·6	2·4
SiO <sup>2</sup> . . . . .	60·0	60·4	59·6	53·55	45·6	71·6	62·5	69·6	62·0
P <sup>2</sup> O <sup>5</sup> . . . . .	0·4								
	99·0	100·0	99·4	100·00	100·0	97·0	97·4	99·4	99·3

**Window-glass.**—Approximately =  $\text{Na}^2\text{O} \cdot 2\text{SiO}^2 + \text{Ca}^2\text{O} \cdot 2\text{SiO}^2$ . *a* to *f*, French, *g*, English. *f* and *g* the hardest and most infusible; *b* the next; *d* the softest and most easily fused of the whole. In France a mixture is used of 100 pts. of quartz-sand with between 30 and 40 pts. of dry carbonate of sodium (or as much sulphate with charcoal) and 30 to 40 parts of carbonate of calcium. (Dumas.)

	<i>a</i> .	<i>b</i> .	<i>c</i> .	<i>d</i> .	<i>e</i> .	<i>f</i> .	<i>g</i> .
Na <sup>2</sup> O . . . . .	15·22	11·30	12·88	17·70	13·7	10·1	11·1
Ca <sup>2</sup> O . . . . .	13·31	17·25	16·17	9·65	7·8	14·3	12·5
Al <sup>2</sup> O <sup>3</sup> . . . . .	1·82	2·20	2·40	4·00	10·0	7·6	7·4
SiO <sup>2</sup> . . . . .	69·65	69·25	68·55	68·65	68·5	68·0	69·0
	100·00	100·00	100·00	100·00	100·0	100·0	100·0

**German Window-glass** generally consists of a double silicate of calcium and potassium, e.g. 100 pts. of quartz-sand, 50 pts. of pearlash, from 25 to 30 pts. of chalk, and 2 pts. of nitre. In many mixtures, however, common salt is an ingredient; or it is really a *Glauber's salt glass*, which, according to Gehlen, is prepared with 100 pts. of quartz-sand, 50 pts. of dry Glauber's salt, 17·5 to 20 pts. of lime, and 4 pts. of charcoal.

**French Mirror-glass.**—Specific gravity, 2·488—2·506. About =  $2(\text{Na}^2\text{O} \cdot 3\text{SiO}^2) + \text{Ca}^2\text{O} \cdot 3\text{SiO}^2$ . The variety *a* examined by Berthier, *b* by Tassaert, *c* and *d* by Dumas. All the varieties have a bluish tinge arising from the soda (*d* the least), from which the glass containing potash is free.

**Venetian Mirror-glass.**—About =  $\text{K}^2\text{O} \cdot 3\text{SiO}^2 + 2(\text{Na}^2\text{O} \cdot 3\text{SiO}^2) + 3(\text{Ca}^2\text{O} \cdot 2\text{SiO}^2)$ ; *e*, obtained from an old mirror of a somewhat yellow colour. (Berthier.)

**Bohemian Glass.**—Specific gravity, 2·396; containing about  $2(\text{K}^2\text{O} \cdot 3\text{SiO}^2) + 3(\text{Ca}^2\text{O} \cdot 3\text{SiO}^2)$ ; *f* obtained from a goblet from Neufeld in Bohemia, transparent and colourless (Berthier); *g* from Neufeld (Gros); *h* from an old cup of Bohemian glass, perfectly transparent (Dumas); *i*, ordinary Bohemian glass. (Peligot.)

**k. English Crown-glass**, of specific gravity 2·487, has a composition similar to that of Bohemian glass.



	a.	b.	c.	d.	e.	f.	g.	h.	i.	k.
K <sup>2</sup> O . . . . .				5.50	6.9	12.7	11.0	11.8	15	21.0
Na <sup>2</sup> O . . . . .	17.0	17.0	17.5	12.05	8.1	2.5				
Ca <sup>2</sup> O . . . . .	6.4	6.0	3.8	5.60	11.0	10.3	10.0	9.2	8	9.9
Mg <sup>2</sup> O . . . . .					2.1		2.3			
Mn <sup>2</sup> O . . . . .					0.1	0.2	0.2			
Fe <sup>2</sup> O <sup>3</sup> . . . . .					0.2	0.3	3.9			
Al <sup>2</sup> O <sup>3</sup> . . . . .	2.6		2.8	3.50	1.2	0.4	2.2	9.6	1	1.4
SiO <sup>2</sup> . . . . .	72.0	76.0	75.9	73.85	68.6	71.7	71.6	69.4	76	67.7
	99.1	100.0	100.0	100.50	98.2	98.1	101.2	100.0	100	100.0

*Crystal glass.*—Specific gravity, 2.9 to 3.255, from trisilicate to tetrasilicate of lead and potassium. Pure silicate of lead is yellow; but when it is combined with a sufficient quantity of silicate of potassium, the mixture is colourless. This glass is obtained from 100 pts. of pure quartz-sand, 60 to 70 pts. of minium or litharge, and 30 to 40 pts. of purified pearlsh; sometimes an addition is made of 4 pts. of borax, 3 pts. of nitre, 0.15 pts. of arsenious acid, and 0.2 pts. of peroxide of manganese.

a. *London Crystal glass.*—Transparent and colourless; used in the construction of philosophical instruments; containing about  $2(K^2O.4SiO^2) + 3(Pb^2O.4SiO^2)$  examined by Berthier.

b. From Vonèche in Belgium;  $K^2O.4SiO^2 + 2(PbO.4SiO^2)$ , nearly. (Berthier.)

c. From Newcastle;  $2(K^2O.3SiO^2) + 3(Pb^2O.3SiO^2)$ , nearly. (Berthier.)

d. Origin unknown;  $2(K^2O.3SiO^2) + Ca^2O.3SiO^2 + 3(Pb^2O.3SiO^2)$ , nearly, analysed by Dumas.

e. English;  $K^2O.3SiO^2 + Pb^2O.3SiO^2$ , nearly; analysed by Faraday.

*Flint-glass.*—Acid silicate of lead and potassium, prepared from the purest materials possible: for example, 100 pts. of quartz, 50 pts. of pearlsh, 100 pts. of minium, 3 pts. of borax, 0.15 pt. of arsenious acid, and 0.2 pt. of peroxide of manganese. Guinand's flint glass has a specific gravity of 3.3 to 3.6; Frauenhofer's, a specific gravity of 3.77. a. Flint glass examined by Faraday. b. Guinand's flint glass, analysed by Dumas,  $= 2(K^2O.2SiO^2) + 3(Pb^2O.2SiO^2)$ . Döbereiner (Schw. J. liv. 424) recommends the proportions of 1 at. of potash to 2 at. of oxide of lead and 7 at. of silica. Faraday's flint glass (Pogg. Ann. xviii. 615), specific gravity = 5.44, has a very different composition, being a compound of oxide of lead with silicic and boracic acids.

	Crystal glass.					Flint glass.		Strass.
	a.	b.	c.	d.	e.	a.	b.	
K <sup>2</sup> O . . . . .	9.0	6.6	9.4	8.9	13.67	11.75	11.7	7.9
Ca <sup>2</sup> O . . . . .				2.6			0.5	
Pb <sup>2</sup> O . . . . .	28.2	34.4	37.4	32.5	33.28	43.05	43.5	53.0
Mn <sup>2</sup> O . . . . .	1.0			trace.				
Fe <sup>2</sup> O <sup>3</sup> . . . . .	0.4		0.8					
Al <sup>2</sup> O <sup>3</sup> . . . . .		1.0	1.2				1.8	1.0
SiO <sup>2</sup> . . . . .	59.2	56.0	51.4	56.0	51.93	44.30	42.5	38.1
	97.8	98.0	100.2	100.0	98.88	99.10	100.0	100.0

The *Mentz Flux*, or *Pierre de Strass*, used in the formation of artificial gems consists of flint glass with a smaller proportion of silicate of potassium, prepared likewise with the purest ingredients: e.g. 100 parts of quartz or rock-crystal, 32 to 52 parts of hydrate of potassium purified by alcohol, 154 to 157 parts of minium, or 171 parts of pure white lead, 6 to 9 parts of borax,  $\frac{1}{4}$  to  $\frac{1}{2}$  part of arsenious acid. Dumas analysed the *Strass* manufactured by Donault-Weiland, the composition of which is nearly  $= K^2O.2SiO^2 + 3(Pb^2O.2SiO^2)$ .

The flint glass b contains also a trace of arsenious acid, and the *Strass* a trace of borax in addition.

*Aventurin glass.*—A brownish-coloured glass, interspersed with small spangles, which give it a peculiar shining appearance. (See vol. i. p. 476.)

*Ruby glass, containing Gold.*—Splittgerber (Pogg. Ann. lxi. 144) gives the following proportions, as affording an excellent glass of this kind: 3 lbs. 4½ oz. of fine white sand, 1 lb. 14 oz. of nitre, 1 lb. 13 oz. of pure white soda, 4 oz. of carbonate of calcium, 2½ oz. of arsenious acid, 4½ oz. of minium, 4 oz. of antimony-glass (i. 322), and the solution of a Dutch ducat, weighing 3.41 grammes, in aqua regia. The gold-solution is first poured into the sand; the remaining ingredients are then added, and the whole is put into a glass-pot and exposed for more than three hours to a white heat. This method differs from former ones, in not having any purple of Cassius or oxide of tin added, those materials having hitherto been always

considered necessary. The glass thus obtained is perfectly colourless, but on being heated to a temperature of  $500^{\circ}\text{C}$ . ( $932^{\circ}\text{F}$ .), assumes an intense ruby colour. The colour, when once produced, cannot be again destroyed by exposure to heat, even in an atmosphere of oxygen or hydrogen, or in a close crucible surrounded with sand, powdered charcoal, or oxide of zinc, or by throwing the glass into a flux of nitre or chlorate of potassium; before the oxyhydrogen blow-pipe, however, it loses its colour, but regains its original tint on cooling and subsequent exposure to heat. Splittgerber accounts for the peculiarities of this glass by assuming that the gold in the colourless variety is in the form of trioxide; and that, when heated a second time, it is converted into the ruby-red oxide described by Berzelius, in consequence of a portion of its oxygen combining with one or more of the other substances present—probably with the antimonious oxide. The slight increase in bulk consequent on the second heating appears to be in favour of this view. Splittgerber likewise succeeded in obtaining a coloured glass with purple of Cassius, but of a violet rather than a ruby tint. Rose (Pogg. Ann. lxxii. 556) gives the following proportions for ruby-coloured glass: 46 lbs. of fine quartz, 12 lbs. of borax, 12 lbs. of nitre, 1 lb. of minium, 1 lb. of white arsenious acid, and a solution of 8 ducats in aqua regia. The whole is then mixed and fused as before. The resulting glass is colourless, but when again heated to redness acquires a ruby colour; Rose has likewise observed that the red colour is produced, whether the glass is heated in atmospheric air, oxygen, or carbonic acid gas. If exposed to a heat at which it softens, it becomes opaque and liver-coloured. When it is fused before the oxyhydrogen blowpipe, colourless drops are obtained, which Rose could not again obtain of a red colour by heating. Rose is of opinion that the colourless glass contains silicate of gold, and that this compound, when heated, is decomposed, with separation of oxide of gold, which imparts the red colour to the glass; moreover, that the liver-coloured glass probably contains metallic gold.

a. Aventurin from Venice, analysed by Gahn. b. Analysed by Peligot. c. By Kersten. d. Ruby-glass, analysed by Splittgerber, the gold found by experiment amounting to less than one-half the quantity per cent. added. e. Venetian ruby-glass, in the form of flattened round masses, distinguished from the ordinary varieties by being very fusible, and not losing its red colour when melted; analysed by Böhme. (J. pr. Chem. xxxviii. 335.)

	Aventurin glass.		c.	Ruby Glass.	
	a.	b.		d.	e.
K <sup>2</sup> O . . .	2.1	5.5	5.3	} 23.41 {	6.70
Na <sup>2</sup> O . . .	8.2	7.1	7.0		5.79
Ca <sup>2</sup> O . . .	8.0	8.9	9.0	2.01	3.80
Mg <sup>2</sup> O . . .	4.5				0.50
Fe <sup>2</sup> O <sup>3</sup> . .	6.5	Fe <sup>2</sup> O 3.5	Fe <sup>2</sup> O <sup>3</sup> 2.4		2.20
Al <sup>2</sup> O <sup>3</sup> . . .		traces.			
SiO <sup>2</sup> . . .	65.2	67.7	67.3	64.17	58.98
P <sup>2</sup> O <sup>5</sup> . . .	1.5				
Cu . . .	3.0	3.9	4.0		
Sn . . .	traces	SnO <sup>2</sup> 2.3	2.3		SnO <sup>2</sup> 0.69
Sb . . .				2.40	
As . . .					traces.
Pb . . .		1.1	1.0	5.06	22.93
Au . . .				0.06	0.40
	99.0	100.0	98.3	97.11	101.99

*Enamel* is, for the most part, a double silicate of lead and potassium, rendered opaque by stannic oxide. In one specimen of enamel, Dumas found 8.3 per cent. of potash, 60.3 of oxide of lead, 9.8 of stannic oxide, and 31.6 of silica. Antimonious or arsenious acid produces a similar effect to the stannic oxide. By adding colouring agents, principally metallic oxides, to white enamel, the coloured varieties are obtained (p. 487).

For further details on the composition and manufacture of glass, see *Uré's Dictionary of Arts, Manufactures and Mines*, ii. 339; Payen, *Précis de Chimie Industrielle*, 4me édition, i. 489; Regnault, *Cours de Chimie*, ii. 332; Pelouze et Frémy, *Traité de Chimie Générale*, 3me édition, ii. On porcelain colours for enamel, Wächter (Ann. Ch. Pharm. lxi. 99).

*Decomposition of Glass.*—1. Water extracts potash or soda from glass, together with a portion of silica, the decomposition taking place with greater ease in proportion as the glass is richer in these alkalis, and more minutely divided, and the temperature of the water higher. The powder filed off from a tube of white glass reddens moistened turmeric-paper (Bischof, Kastn. Arch. i. 443). Finely powdered plate-glass

acts in a similar manner (Faraday, Pogg. Ann. xviii. 669). Water triturated with powdered glass in an agate mortar becomes alkaline, and on the addition of sal-ammoniac deposits flakes of silica (Fuchs, Kastn. Arch. v. 306). Water becomes alkaline after long digestion with glass at the boiling heat, and likewise turbid, from separation of an insoluble silicate of calcium (Dumas). An alkaline reaction is exhibited by the powder of bottle-glass, and of Reaumur's porcelain, formed from it; also of plate-glass, crown-glass, flint-glass, and white enamel. After sufficient washing it no longer reddens turmeric-paper, unless it be recrushed in a mortar. One hundred parts of finely divided flint-glass boiled for a week with water, lose 7 pts. of potash, which may be obtained in the solid state by evaporation (Griffiths, Quart. J. of Sc. xx. 258). The moisture in the atmosphere produces a similar alteration, separating the potash and soda, and leaving the greater part of the silica with the lime on the surface of the glass; glass thus decomposed often exhibits prismatic colours on its surface. Sometimes this superficial decomposition is scarcely visible; but, on warming the glass, numerous fine scales peel off, and leave the surface dull, opaque, and wrinkled. This fault shows itself in glass, to which, for the sake of economising fuel, too small a quantity of silica has been added. The pearly stratum with which specimens of antique glass found buried in the earth are covered consists almost wholly of silica (Griffiths). Glass which has lain in pits at least ten feet deep in the ground, is soft when dug up, and may be bent and indented, and even cut in two with a knife; but after exposure to the air for a few hours, it again hardens, and if it has been previously bent or twisted, it becomes extremely brittle, like unannealed glass. (Col-ladon, J. Chim. méd. xvi. 579.)

2. All kinds of glass are corroded by *hydrofluoric acid*, with formation, partly of fluoride of silicium, and partly of the double fluorides of silicium and potassium, sodium, calcium, &c. A hot concentrated solution of phosphoric acid also decomposes every variety. Glass which is poor in silica is attacked by boiling *oil of vitriol*; and glass of yet inferior quality—that, namely, which becomes dull on exposure to heat (Dumas)—is acted on by boiling *hydrochloric* and *nitric acids*, and *aqua-regia*, a dull spot remaining after evaporation of the acid (Berzelius). The acids dissolve out potash, soda, lime, and other bases, and separate the silica. On powdered glass they act with far greater energy. From pulverised flint-glass boiling hydrochloric acid extracts potash only, not the oxide of lead (Griffiths). Many kinds of bottle-glass which resist the action of acetic acid are decomposed by the stronger mineral acids; thus a bottle filled with sulphuric acid will sometimes, at ordinary temperatures, gradually become covered with warty depressions, which at last penetrate through the substance of the glass (Dumas). In distilling hydrochloric acid from a green glass retort, Hess (Pogg. Ann. xx. 540) obtained a crystalline sublimate [?] of silica, while chloride of potassium, sesquioxide of iron, and silica were dissolved. Many anhydrous salts of ammonia containing the stronger acids, also attack glass—especially lead-glass—when heated in contact with it; such is the case with a mixture of hydrochlorate and nitrate of ammonium (Silliman), or the neutral or acid sulphate of ammonium. (Marchand, Pogg. Ann. xlii. 556.)

3. Solutions of *potash* and *soda* dissolve out the silica of glass with greater ease in proportion to their temperature and degree of concentration. Even at ordinary temperatures, the alkaline liquid partially dissolves the glass bottle in which it is preserved, frequently causing it to crack. Even ammonia attacks many kinds of glass; a bottle made of flint-glass, and containing a solution of carbonate of ammonia, became so fragile that, on shaking it, pieces of glass were detached. (Griffiths.)

4. Glass containing lead blackens when heated in the flame of a lamp or in hydrogen gas, from reduction of the lead—and when heated in sulphuretted hydrogen, from formation of sulphide of lead. On this account Guinand's flint-glass (p. 841) becomes tarnished in dwelling-houses (Faraday). A bottle made of French glass, in which sulphurate of ammonium had been kept, acquired a metallic lustre, from formation of sulphide of lead. (Bischof, Br. Arch. xvii. 242.)

*Crystallised or Devitrified Glass.*—a. Many kinds of glass, when slowly cooled in the pots, separate into two portions, the one crystallising in opaque prisms and needles, the other retaining its vitreous character. According to the following analysis by Dumas, it appears that the portion which crystallises gives up soda to that which remains in the vitreous state.

	Crystallised portion.	Vitreous portion.
Na <sup>2</sup> O . . . . .	14.9 . . .	19.8
Ca <sup>2</sup> O . . . . .	12.0 . . .	12.0
Al <sup>2</sup> O <sup>3</sup> . . . . .	4.9 . . .	3.5
SiO <sup>2</sup> . . . . .	68.2 . . .	64.7
	100.0	100.0



*b. Reaumur's Porcelain.*—Many kinds of glass, after exposure for several hours to a heat at which they become soft—for example, in a potter's furnace—pass into a condition resembling porcelain. Bottle glass is the most disposed to undergo this change, doubtless from the greater quantity of alumina which it contains; next in order is the more common sort of green window glass; white glass rich in lime is also liable to this change, but not pure silicate of potassium or sodium, or lead-glass. (Lewis, Dartigues.)

The devitrification takes place just as well if the glass vessels are surrounded within and without with an infusible powder or cement, to prevent them from losing their shape—*e. g.* sand, a mixture of sand and gypsum, bone-ash, clay, powdered bricks, lime, sesquioxide of iron, charcoal, or soot,—as when they are heated by themselves; but in the former case, a longer time is required (Lewis, Dartigues, Morveau). It occurs also in a similar manner with glass enveloped in a lava-stream (Morveau). This change may either be regarded, according to Dartigues' supposition, as arising simply from the amorphous glass passing without change of composition into the crystalline state—the long continued state of softness affording the atoms an opportunity of uniting together in crystalline molecules; or we may suppose with Lewis, Morveau, and Dumas, that the glass, in undergoing this change, loses a portion of its alkali, which, when the glass is ignited by itself, passes off in vapour, and when it is surrounded by a powder during ignition, is absorbed by the powder. Dumas is likewise of opinion that the protoxides of manganese and iron present in the glass are peroxidised at the same time. According to Lewis, the sand surrounding the glass as cement becomes caked together by absorbing alkali. Dumas found in a devitrified specimen of bottle glass only 2 per cent. of potash, together with 27.4 per cent. of lime, 6.6 of the peroxides of manganese and iron, 12.0 of alumina, and 52.0 of silica. [The behaviour of Reaumur's porcelain in fusing is also in favour of this theory; *vid. seq.*]

In this change, the following facts are to be distinguished:—1. The glass first becomes cloudy, and appears blue by reflected and yellow by transmitted light (Lewis, Fournet), still, however, exhibiting a vitreous fracture. The blue colour is also seen at the fractured edges, and consequently cannot proceed from oxidation (Fournet). The opacity doubtless arises from the separation of fine particles, whose composition differs from that of the rest of the mass. Many iron slags behave in a similar manner (especially the double silicate of aluminium and calcium). Many slags which appear green when cooled rapidly, become blue within and yellow by transmitted light when slowly cooled, even if they are green on the outside, but the powder again assumes a green colour. This fact would appear to explain the action of the test which is employed to distinguish a great many earths and heavy metallic oxides by the blowpipe; viz. that the bead obtained by fusing them with borax or microcosmic salt, remains clear when rapidly cooled, but becomes turbid and opaque by exposure to *interrupted blasts*, or *flaming*, whereby it is kept for a long time in a soft state, and crystalline compounds are produced and separated. (Fournet, *Ann. Ch. Phys.* lxxix. 370; also *J. pr. Chim.* xxvi. 331.)

2. After this stage, white, opaque needles are formed, proceeding from the inner and outer surfaces of the glass, and finally meeting in the centre. The place of contact is often marked by a brown line. The mass thus far changed is *Reaumur's porcelain*. When burnt between pipe-clay, it has a smooth surface, but if burnt between lime or bone-ash, it acquires a rough, wrinkled, or blistered surface. When burnt between powdered charcoal, its surface becomes black or grey (Lewis). It is white and nearly opaque, appearing at the fractured surface to possess a straight fibrous texture; it is specifically heavier than glass, and so hard that it scratches glass and sometimes even rock-crystal, and emits sparks with steel; it does not crack so readily with changes of temperature as glass, or even as porcelain, and conducts heat and electricity better than the former, so that, unless insulated, it does not become electrical by friction. Reaumur's porcelain may be used instead of ordinary porcelain in the fabrication of vessels. It fuses with much greater difficulty than glass, and is thereby converted into a white or grey enamel, transparent only at the edges—having a conchoidal fracture, harder than glass, but softer than Reaumur's porcelain. The specific gravity of this enamel is to that of the substance before fusion as 2.625 : 2.801; it does not become electrical by friction. (Morveau.)

3. If the baking be too long continued, the threads of the fasciculated or fibrous structure become separated by fissures, and the whole is converted into a fine-grained and subsequently a coarse-grained mass, loose, greyish, and still more difficult of fusion. When the porcelain has begun to change from the fibrous to the granular condition, it may still be fused by the heat of a forge to a pearly, porous mass, which contains green glass enclosed within. If the change to the fine-grained con-

dition is complete, it fuses to a spongy mass; but when the coarse-grained state is arrived at, it no longer fuses, but cakes together to an exceedingly hard mass, having a dense fracture.

**GLAUBAPATITE.** A mineral from the Mongo islands on the Mosquito coast, where it occurs in geodes of small yellowish-green or brown crystals, consisting of 74 per cent. phosphate of calcium, 15.1 sulphate of sodium, and 10.3 water. (*Rammelsberg's Mineralchemie*, p. 984.)

**GLAUBER SALT.** Sulphate of sodium. (See SULPHATES.)

**GLAUBERITE.** Native sulphate of sodium and calcium,  $\text{NaCaSO}_4$ . It is found crystallised in four-sided prisms, belonging to the monoclinic system, Colour greyish-white and wine-yellow. Lateral planes transversely striated; terminal planes smooth. Fracture foliated or conchoidal, Hardness = 2.5 to 3. Specific gravity = 2.64 to 2.85. Lustre vitreous. Streak white. Taste slightly saline. Before the blowpipe it decrepitates, and melts to a white enamel. Becomes opaque when immersed in water. It is found in crystals in rock-salt at Villa Rubia, near Oçana, in New Castile; also at Aussee, in Upper Austria, in Bavaria, at the salt mines of Vic in France, and in the province of Tavapaca, Peru. (*Dana*, ii. 374.)

**GLAUCINE.**  $\text{C}^{\text{H}}\text{N}^{\text{H}}$  (?). According to Völckel, sulphocyanate of ammonium heated to  $300^{\circ}\text{C}$ . yields, among other products, a compound called *poliene*,  $\text{C}^{\text{H}}\text{N}^{\text{H}}$ ; and this, when heated, gives off 1 at. ammonia,  $\text{NH}_3$ , and is converted into glaucene. (See SULPHOCYANATES.)

**GLAUCIC ACID.** The name originally given to the acid of *Glaucium flavum*, now known to be fumaric acid.

**GLAUCINE.** An alkaloid obtained by Probst from the leaves of the yellow horned poppy (*Glaucium flavum*), a plant growing on sandy sea-shores. It is not contained in the flowers or the root of the plant. It may be extracted by macerating the leaves with acetic acid; boiling the acid juice to coagulate the chlorophyll; treating the clarified liquid with nitrate of lead; decomposing the precipitate with sulphuretted hydrogen; precipitating the filtered liquid with decoction of oak-bark; mixing this precipitate with lime while still moist, after washing and pressing; treating the mixture at a gentle heat with alcohol; passing carbonic acid gas through the alcoholic filtrate, to precipitate the lime; driving off the alcohol by evaporation; and treating the residue with water. Glaucine then remains undissolved, and may be purified by solution in boiling water.

From its aqueous solution it separates by spontaneous evaporation in colourless crusts, composed of nacreous scales; the ethereal solution deposits it in a pitchy mass. From the solutions of its salts it is precipitated by ammonia, as a curdy mass, which after some time becomes pitchy, and melts to an oil at the temperature of boiling water. Its taste is harsh and bitter. It is moderately soluble in hot water, freely in alcohol and ether; the solution blues reddened litmus.

Glaucine decomposes at high temperatures; heated with sulphuric acid, it assumes a fine violet colour; the product forms with water a deep red solution, from which ammonia throws down a deep indigo-blue precipitate. Glaucine is quickly decomposed by nitric acid.

Glaucine forms neutral salts, which have an acrid burning taste, and are precipitated by tincture of galls. The *hydrochlorate* and the *sulphate* are crystalline, very soluble in water and alcohol, insoluble in ether. The *phosphate* crystallises readily (Probst, *Ann. Ch. Pharm.* xxxi. 241.)

**GLAUCIUM FLAVUM.** The yellow horned poppy. The seeds of this plant, after drying in the air, give off 8 per cent. water at  $110^{\circ}\text{C}$ . The seed dried at this temperature contains 42.6 per cent. oil. The stems (air-dried?) yielded 4.6 per cent., the seeds, 9.32 per cent. ash, containing in 100 parts:

	$\text{CO}_2$	$\text{SO}_3$	$\text{P}_2\text{O}_5$	$\text{SiO}_2$	$\text{NaCl}$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{CaO}$	$\text{MgO}$	$\text{Fe}_2\text{O}_3$	$\text{Mn}_2\text{O}_3$	Sand & $\text{O}_2$ loss.
Stem .	6.39	5.89	2.40	4.15	29.14	13.82	..	29.00	3.35	0.82	0.02	5.02
Seed .	22.39	0.76	11.29	2.76	1.07	5.86	1.69	38.22	5.95	5.22	0.70	4.19

(Cloez, *Institut*, 1860, p. 124; *Ann. Ch. Phys.* [3] lix. 129.) The plant contains fumaric acid and two alkaloids—viz. glaucine in the leaves, glaucopirine in the root.

**GLAUCODOTE.**  $(\text{Co}; \text{Fe})\text{S} \cdot (\text{Co}; \text{Fe})\text{As}$ .—A mineral resembling mispickel in crystalline form and in composition, excepting that the iron is partly replaced by cobalt. It crystallises in prisms belonging to the rhombic system. Cleavage very distinct, parallel to the base, less so parallel to the prismatic faces; also massive. Hardness



= 5. Specific gravity = 5.975 to 6.003. Lustre metallic. Colour greyish tin-white. Streak black. It occurs in chlorite slate with cobaltine in the province of Huasco, Chile, and with a pale yellow calcite at Orowitza, in the Bannat. It contains:

	S	As	Co	Fe	Ni	
From Chile . . .	20.21	43.20	24.77	11.90	trace	= 100.08 Plattner.
„ Orowitza. . .	19.78	43.63	32.02	4.56	..	= 99.99 (Patena).

Before the blowpipe it gives the reactions of sulphur, arsenic, cobalt, and iron. (Dana, ii. 63.)

**GLAUCOLITE.** Syn. with SCAPOLITE.

**GLAUCOMELANIC ACID.** A product of the decomposition of ellagic acid (p. 484).

**GLAUCONITE.** A silicate of iron, occurring in green, translucent, opalescent rounded grains in the greensand of various localities. According to Ehrenberg (Berl. Akad. Ber. 1854, pp. 374-384; 1855, pp. 86-172; Jahresb. d. Chem. 1854, p. 885), these grains consist of the stony nuclei and silicified shells of polythalamia. Their composition is somewhat variable, as the following analyses will show:—a. From Gay Head, Massachusetts, by S. L. Dana (*Dana's Mineralogy*, ii. 288); b. From Canley's Pits, Woodtown, New Jersey, H. B. Rogers (*ibid.*); c. From the green sandstone between Dortmund and Witten, Westphalia. (Von der Marck, Jahresb. d. Chem. 1855, p. 1007.)

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Mg <sub>2</sub> O	Ca <sub>2</sub> O	K <sub>2</sub> O	H <sub>2</sub> O	
a. 56.70	13.32	20.10	1.18	1.52	..	..	..	= 92.92
b. 48.45	6.30	24.31	..	trace	12.01	8.40	..	= 99.47
c. 53.46	5.00	21.78	6.21	..	8.79	4.76	..	= 100.00

A green ferrous silicate imbedded in the calcspar of Takkli, near Nagpur, in Central India, appears to have the composition of glauconite. (T. L. Houghton, Phil. Mag. [4] xvii. 16.)

**GLAUCOPHANE.** See WICHTYN.

**GLAUCOPICRINE.** An alkaloid contained in the root of *Glaucium flavum*. It is extracted by exhausting the root with acetic acid; precipitating by ammonia; redissolving the precipitate in acetic acid; precipitating the solution with decoction of oak-bark; treating this precipitate with lime and alcohol, as described in the preparation of glaucine; exhausting the alcoholic residue with ether; evaporating the ethereal solution; treating the residue with a very small quantity of ether, which leaves pure glaucopidine undissolved; and crystallising from boiling water.

Glaucopidine forms granular crystals soluble in water and alcohol, especially when hot; less soluble in ether. Its salts have an extremely bitter and nauseous taste. Animal charcoal removes the glaucopidine from their solutions. Glaucopidine, or any of its salts, heated with strong sulphuric acid, yields a dark green pitchy product, insoluble in water, acids, and ammonia.

Hydrochlorate of glaucopidine crystallises in rhomboïdal plates or in bundles of prisms, soluble in water, insoluble in ether. The sulphate and phosphate are likewise crystallisable. (Probst, Ann. Ch. Pharm. xxxi. 254.)

**GLAUCOSIDERITE.** Syn. with VIVIANITE.

**GLECHOMA.** The herb of ground ivy (*Glechoma hederacea*) at the flowering time contains a tannic acid which turns iron-salts green, also acetic acid, tartaric acid, sugar, gum, volatile oil, waxy and oily substances, an acid and a slightly bitter substance, &c. 1000 pts. of the flowering herb lost by drying, 824 pts. water; the residue yielded to ether 24 pts., then to alcohol 8 pts., then to water 56 pts., to hydrochloric acid 16 pts., and there remained 72 pts. of insoluble vegetable fibre (J. B. Euz, Vierteljahrsschr. pr. Pharm. x. 11.)

**GLIADIN.** See GLUTEN.

**GLINKITE.** A greenish variety of olivine from a talcose slate in Perm, Russia; also occurring in gneiss at Tunaberg in Sweden, with augite and garnet, and in veins 3 inches thick in the mica slate of Kytshimsk, north of Miask in the Ural. (See OLIVINE.)

**GLOBULARIA.** According to G. F. Walz (N. Jahrb. Pharm. xiii. 281), the leaves of *Globularia Alypum* contain a yellow colouring matter, a peculiar tannic acid, globularitannic acid, whose lead-salt dried at 100° C. contains C<sup>20</sup>H<sup>12</sup>PbO<sup>8</sup>; a resin, globulararesin, C<sup>30</sup>H<sup>20</sup>O<sup>3</sup>, having a very strong and fragrant odour, and a bitter principle, globularin, C<sup>30</sup>H<sup>40</sup>O<sup>14</sup>, which is resolved by dilute sulphuric acid into globularetin, C<sup>20</sup>H<sup>14</sup>O<sup>8</sup> (a white pulverulent substance which melts to a resin when heated), paralarotin, C<sup>12</sup>H<sup>10</sup>O<sup>4</sup> (a slightly coloured pulverulent substance insoluble in ether



and precipitated by water from its alcoholic solution), and glucose, with elimination of 1 at. water:



For details respecting these compounds, see *Gmelin's Handbook*, xv. 38; xvi. 82.

**GLOBULIN, or CRYSTALLIN.** (Lehmann, *Physiol. Chem.* i. 366; *Handw.* 2\* Aufl. ii. 134.—*Gerh.* iv. 450.)—An albuminous substance existing in the crystalline lens of the eye, and, according to Berzelius and others, in the corpuscles of the blood. As however it has never been obtained from the latter source free from colouring matter, the identity of the two substances cannot be considered as quite established, more especially as the albuminous substance obtained from the blood-corpuscles by Lehmann's latest process differs essentially from that in the crystalline lens. (See *HÆMATO-CRYSTALLIN*.)

From the crystalline lens, globulin is obtained by triturating this body with water, evaporating the filtered liquid at a temperature below 50° C. and purifying the dry residue by digestion, first with ether, then with dilute alcohol. In the lens of the human eye, Berzelius found 35.9 per cent. of dry globulin.

Globulin thus prepared is a yellowish transparent mass which swells up in water and dissolves, for the most part, forming a gummy liquid. The solution becomes opaline at 73° C., and deposits a coagulum at 93°, therefore at a temperature considerably above that at which albumin coagulates (i. 65). Mixed with a small quantity of acetic acid, it becomes opaline, and deposits a coagulum at 50°; but a larger quantity of acetic acid either prevents the coagulation altogether, or renders a temperature of 100° necessary to produce it. The aqueous solution has a slight alkaline reaction and behaves with mineral acids and metallic salts, in most respects, like a solution of albumin. According to Lehmann, the solution acidulated with acetic acid is precipitated by ammonia, and a solution mixed with ammonia gives a precipitate when cautiously neutralised with acetic acid. Moreover, on passing carbonic acid gas through the aqueous solution, a precipitate is obtained which is soluble in pure water.

The chemical composition of globulin is sensibly the same as that of albumin. Mulder found it to contain on the average, 64.35 per cent. C, 7.0 H, 16.5 N, and 0.3 to 1.2 S. Lehmann found 1.1 per cent. sulphur.

According to Lehmann, globulin from the crystalline lens yields by incineration 0.24 per cent. phosphates, and 1.55 per cent. soluble salts, consisting of alkaline chlorides, sulphates, and phosphates, but no alkaline carbonate (whereas the albumin of serum or white of egg always yields alkaline ash). But the liquid separated by filtration from coagulated globulin yields an ash containing alkaline carbonate. According to the same chemist also, globulin when coagulated by heat gives off ammonia, and the filtered liquid, instead of exhibiting increased alkaline reaction, like white of egg similarly heated, is found to have an acid reaction. Hence Lehmann concludes that soluble globulin contains ammonio-acidic phosphate, which is resolved by heat into ammonia and acid phosphate of sodium. He is also of opinion that globulin contains, in combination with soda, an organic acid—probably lactic acid—to which is due the alkaline ash obtained from the liquid filtered from coagulated globulin. The presence of different mineral salts in albumin and in globulin may perhaps account for the slight differences observed in the characters of the two bodies.

According to Valenciennes and Frémy (*Compt. rend.* xlv. 1122), the outer and inner portions of the crystalline lens of the eyes of mammalia contain different modifications of serum, and those of fishes contain another albuminous substance called phacolin. (See *EYE*, p. 616.)

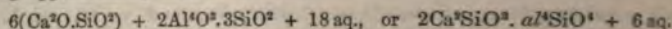
**GLOCKERITE.** A basic ferric sulphate,  $2\text{Fe}^{\text{O}}\text{O}^{\text{H}}\text{SO}^{\text{H}} + 6 \text{ aq.}$ , occurring in stalactites of considerable size at Obergrund near Zuckmantel in Austrian Silesia. (See *SULPHATES*.)

**GLONIN.** Syn. with NITROGLYCERIN. (See *GLYCERIN*.)

**GLOSSECOLITE.** (Shepard, *Sill. Am. J.* [2] xxiv. 124; Pisani, *Compt. rend.* 41, 310.)—A silicate of aluminium from Rising Fawn, in Dade County, Georgia, compact, with conchoidal fracture, dull, of white, yellowish, or brownish colour, with shining streak; adheres to the tongue. Hardness = 2 to 2.5. Specific gravity = 2.2 (or if protected from penetration of water, 1.7). Soft to the touch and very brittle. Heated in a tube, it gives off water (17 per cent. according to Shepard, 21.8 according to Pisani), and turns bluish-grey. Infusible before the blowpipe; exhibits a fine blue colour with cobalt-solution. Decomposed by heating with sulphuric acid. Shepard regarded it as an opal; but according to Pisani's analysis, it contains 40.4 per cent.  $\text{SiO}_2$ , 37.8  $\text{Al}^{\text{O}}$ , 0.5  $\text{Mg}^{\text{O}}$ , and 21.8 water (= 100.6).

**GLOTTALITE.** A mineral from the greenstone near Port Glasgow, on the Clyde; occurring in cubes with the angles truncated; colourless or white, with vitreous

lustre. According to Thomson's analysis (*Outlines of Mineralogy*, i. 328), it contains 37.01  $\text{SiO}_2$ , 16.31  $\text{Al}_2\text{O}_3$ , 0.50  $\text{Fe}_2\text{O}_3$ , 23.93  $\text{CaO}$  and 21.25 water (= 99.00), agreeing approximately with the formula



Greg (*Minerals of Great Britain*, p. 171) regards the mineral as chabasite, a view which does not accord with Thomson's analysis. The existence of the mineral as a distinct species cannot, however, be considered as positively established. (*Rammelsberg's Mineralchemie*, p. 781.)

**GLUCIC ACID.**  $\text{C}^6\text{H}^{12}\text{O}^9 = \text{C}^{24}\text{H}^{48}\text{O}^{36}$  (Peligot), or  $\text{C}^{16}\text{H}^{32}\text{O}^{24} \cdot 2\text{HO}$  (Rochleder and Kawalier). *Kalisaccharic acid.* (Peligot, *Ann. Ch. Phys.* lxxvii. 154; Mulder, *Ann. Ch. Pharm.* xxxvi. 243; Gerh. ii. 563.)—An acid produced by the action of acids and alkalis on sugar. A solution of dextroglucose (grape- or starch-sugar), saturated with lime or baryta, and left to itself for several weeks, gradually loses its alkaline reaction, and the base which it contains is no longer precipitable by carbonic acid. It then gives with basic acetate of lead, a bulky white precipitate of basic glucate of lead, which, when decomposed by sulphydric acid, yields glucic acid (Peligot). An easy mode of preparing the acid is to mix grape-sugar melted at  $100^\circ \text{C.}$  in its water of crystallisation, with a warm concentrated solution of caustic baryta, potash, or soda. Great rise of temperature then takes place; and if the action be stopped before it has gone too far, a large quantity of glucic acid is obtained, which may be extracted with basic acetate of lead as above. (Persoz.)

Glucic acid may also be prepared by boiling cane-sugar, in contact with the air, with dilute sulphuric acid; filtering; saturating with chalk; evaporating to dryness; and digesting the residue in a very small quantity of water. The brown syrupy liquid thus obtained, which contains acid glucate of calcium, together with the calcium-salt of *apogluccic acid*, a small quantity of sulphate of calcium, and uncrystallisable sugar, is treated with alcohol to precipitate the apogluccate, and decolorised with animal charcoal; then mixed with caustic lime in sufficient quantity to destroy the acid reaction; and again with alcohol, which throws down neutral glucate of calcium in white flakes. From this salt the acid may be obtained by precipitating its solution with basic acetate of lead, as above. (Mulder.)

According to Rochleder and Kawalier (*J. pr. Chem.* lxxiv. 28, 299; *Jahresh.* 1858, p. 257), gallotannic acid boiled with baryta-water yields glucic and gallic acids, and if the liquid, when cold, be filtered to separate the precipitate of gallate of barium, the filtrate shaken up with air, and the rusty-brown precipitate thereby formed be removed, a solution is obtained free from gallic acid; and on removing the baryta by sulphuric acid, precipitating with basic acetate of lead, decomposing the precipitate with sulphydric acid, and evaporating in vacuo, glucic acid remains in the form of a thick acid syrup.

Glucic acid (from sugar), obtained from its solution by evaporation in vacuo, is a colourless, amorphous body, resembling tannin, very soluble in water and in alcohol; that obtained from tannic acid does not solidify (Kawalier). According to Mulder it does not absorb moisture from the air, but according to Peligot, it is highly hygroscopic when dry. It has a very fresh taste. Heated to  $100^\circ \text{C.}$ , it decomposes, turning brown, and giving off a large quantity of water. The aqueous solution turns brown when boiled in contact with the air, or with dilute sulphuric or hydrochloric acid, forming apogluccic acid. With the same acids in the concentrated state, it forms a brown ulmic substance insoluble in water.

The *glucates*, both acid and neutral, are soluble in water. The *neutral calcium-salt*, dried at  $100^\circ$ , is permanent in the air, and appears to contain  $\text{C}^{12}\text{H}^{24}\text{CaO}^8 + \frac{1}{2}\text{H}_2\text{O}$  (Analysis by Mulder, 38.4 per cent. C, 4.5 H, and 23.2 Ca; calculation, 38.8 C, 4.0 H, and 22.6 Ca). It is very soluble in water, sparingly in alcohol. The aqueous solution is decomposed by carbonic acid, yielding acid glucate and carbonate of calcium.

The *acid calcium-salt* crystallises in needles, soluble in alcohol. It is produced by the action of aqueous glucic acid on carbonate of calcium.

*Basic glucate of lead* is insoluble in water, and appears to contain  $2\text{C}^{12}\text{H}^{24}\text{PbO}^8 \cdot 3\text{PbO} + \text{H}_2\text{O}$ . (Analysis by Peligot, 14.8 and 14.2 C, 1.9 H, 69.3 and 70.5 Pb; calculation, 15.0 C, 1.7 H, and 70.0 Pb.)

**Apogluccic acid**, the product formed from glucic acid by oxidation in the air (p. 848), may be separated from the solution of its calcium-salt by precipitating with acetate of lead, and decomposing the lead-salt with sulphydric acid. In the dry state it forms a brown amorphous mass easily soluble in water, sparingly soluble in alcohol, insoluble in ether. According to Mulder, it contains, when dried at  $120^\circ \text{C.}$ ,  $\text{C}^{14}\text{H}^{28}\text{O}^8 + \text{HO}$ . It is perhaps identical with assamar. (See ASSAMAR, CARAMEL, HUMIC ACID, SUGAR, ULMIC ACID.)

**GLUCINUM.** *Glucium, Beryllium.* Symbol  $G$ ; atomic weight 4.7: or Symbol  $Be$ ; atomic weight 7.

This somewhat rare metal, the oxide of which was discovered by Vauquelin in 1798, occurs as a silicate, either alone, as in phenacite, or associated with other silicates, in beryl, euclase, leucophane, helvite, and several varieties of gadolinite; also as an aluminate in chrysoberyl or cymophane.

Wöhler and Bussy, in 1828, first obtained metallic glucinum, though in an impure and pulverulent state, by fusing the chloride with potassium in a platinum crucible. Becquerel afterwards reduced it in steel-grey crystalline scales by electrolysis of a solution of the chloride; and Debray, in 1854 (*Ann. Ch. Phys.* [3] xlv. 5), obtained it in the compact state by reducing the chloride with sodium, in a manner similar to Deville's first process for the reduction of aluminium. A small dish containing chloride of glucinum is introduced into a combustion-tube, and after the air has been expelled by a current of hydrogen, another small dish containing metallic sodium, previously well cleansed from naphtha by pressure between filtering paper, is likewise introduced. Heat is then applied, first to the sodium to melt it, and then to the chloride of glucinum, which volatilises, and coming in contact with the melted sodium, is thereby decomposed. A black mass consisting of glucinum and chloride of sodium is thus obtained, from which the metal may be separated in distinct globules, by melting the mass in a small crucible with an additional quantity of chloride of sodium, and washing out the soluble salts with water. The improved methods of reducing chloride of aluminium with sodium (i. 160) might doubtless be applied with advantage to the preparation of glucinum.

Glucinum, as obtained by Debray's process, is a white metal, of specific gravity 2.1. It may be forged, and rolled into sheets like gold. Its melting-point is below that of silver. It may be melted in the outer blowpipe-flame, without exhibiting the phenomenon of ignition presented by zinc and iron under the same circumstances; it cannot even be set on fire in an atmosphere of pure oxygen, but in both experiments becomes covered with a thin coat of oxide, which seems to protect it from further change. It does not appear to combine with sulphur under any circumstances, but unites directly with chlorine and iodine with the aid of heat. It unites readily with *silicon*, forming a hard brittle substance susceptible of a high polish; this alloy is always formed when glucinum is reduced in porcelain vessels. Glucinum does not decompose water at a boiling heat, or even when heated to whiteness. *Sulphuric* and *hydrochloric acids* dissolve it, with evolution of hydrogen. *Nitric acid*, even when concentrated, does not act upon it at ordinary temperatures, and dissolves it but slowly at the boiling heat. Glucinum is not attacked by *ammonia*, but dissolves readily in caustic *potash*.

The above-mentioned properties differ considerably from those of the metal which Wöhler obtained by igniting chloride of glucinum with potassium in a platinum crucible, the metal thus produced being a grey powder, very refractory in the fire, but combining with oxygen, sulphur, and chlorine much more energetically than Debray's metal. The differences appear to be due, partly to the different states of aggregation, and partly to the contamination of Wöhler's metal with platinum and potassium.

*Compounds of Glucinum.*—Glucinum forms but one class of compounds, and into these it was supposed by Berzelius to enter as a sesquiatomic radicle (with the atomic weight 7) the chloride being  $Be^2Cl^3$ , and the oxide  $Be^2O^3$ , this view being based upon certain resemblances between the chlorides and hydrates of glucinum and aluminium, and upon the supposed capability of glucinum and aluminium to replace one another in indefinite proportion in minerals, *e.g.* in chrysoberyl. This, however, has been completely disproved by the researches of Awdejew and Damour, from which it appears that the proportions of glucinum and aluminium in chrysoberyl are quite constant, from whatever locality the mineral may be derived. Moreover, glucina bears, on the whole, a much closer resemblance to the protoxides than to the sesquioxides. It forms a carbonate and double carbonates, which alumina does not. When strongly heated it volatilises like magnesia, without fusing, whereas alumina melts; and it cannot be fused with lime, as alumina can, without the presence of another body, such as silica or alumina.

Again, chloride of glucinum does not form definite compounds with the alkaline chlorides as chloride of aluminium does. For these reasons Debray regards glucinum as monatomic, that is, as replacing 1 at. of hydrogen, and assigns to glucina the formula  $G^2O$ .

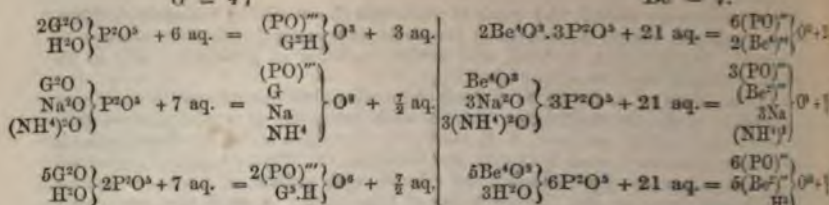
This view of the atomicity of glucinum is further recommended by the greater simplicity of the formulæ which it affords for many of the compounds of the metal; take for example the phosphates analysed by Scheffer (*Ann. Ch. Pharm.* cix. 144):



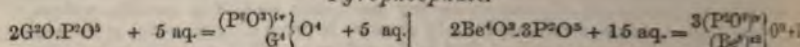
## Orthophosphates.

G = 47

Be = 7.



## Pyrophosphate.



On the other hand, H. Rose (Pogg. Ann. xvi. 445) is disposed to regard glucina as a sesquioxide, partly from certain considerations relating to its specific volume, and further, because when heated with alkaline carbonates, it decomposes them, which a protoxide is known to do. It must also be observed that many compounds of glucinum are not isomorphous with the generality of substances, which, if glucinum be monatomic, must be represented by similar formulae. Thus glucina is not isomorphous with lime or magnesia; chrysoberyl, if expressed by the formula  $\text{Al}^2\text{GO}^2$ , will be included, so far as composition goes, in the class of *spinels*; but in crystalline form, it differs essentially from all other minerals of that class. The emerald,  $\text{GaSiO}^3$ , also differs completely in crystalline form from the generality of silicates of the form  $\text{M}^2\text{SiO}^3$ . Ordway (Sill. Am. J. [2] xxvi. 197) finds that glucina has a great tendency to form basic salts with three and six at. of metal to 1 at. of acid radicle, and adduces this tendency as an argument in favour of the sesqui-equivalent value of the metal; inasmuch as aluminium and ferrium exhibit the same tendency;—but as lead, which is certainly not sesqui-atomic, forms a great number of basic salts of similar constitution, this argument has not much force.

On the whole, the question as to the equivalent value of glucinum cannot be regarded as decided, but the balance of evidence appears to incline in favour of the sesqui-equivalent value.

The affinity of glucina for acids is less than that of the alkaline earths and of yttria, but stronger than that of alumina; for the hydrate decomposes ammoniacal salts at the boiling heat. The hydrate dissolves readily in acids, the ignited oxide slowly, but it may be rendered easily soluble by fusion with sulphate of potassium. The salts are colourless, unless the acid itself is coloured: many of them crystallise well. Most neutral glucinum salts are soluble in water; the solutions have a sweet, astringent taste, and redden litmus. Many glucinum salts which are insoluble in water, e. g. the borate, phosphate, carbonate, &c., dissolve readily in acids. The silicates dissolve in acids only after ignition with sulphate of potassium; by fusing them with caustic alkalis or alkaline carbonates, the glucina is separated, and is then soluble in acids. Glucinum salts containing volatile acids, even the sulphate, give off the acid when ignited; the anhydrous chloride volatilises without decomposition.

Glucina has a great tendency to form basic salts. According to Ordway the neutral nitrate,  $2\text{GNO}^3 + 3\text{H}^2\text{O}$ , or  $\text{Be}^4\text{O}^3.3\text{N}^2\text{O}^5 + 9\text{H}^2\text{O}$ , heated for 20 hours over the water-bath, leaves a soluble basic nitrate containing  $\text{G}^4\text{O}.2\text{GNO}^3 + 3\text{H}^2\text{O}$  or  $2\text{Be}^4\text{O}^3.3\text{N}^2\text{O}^5 + 9\text{H}^2\text{O}$ ; the same salt remains in solution when an aqueous solution of the neutral nitrate is treated in the cold with carbonate of barium, but on boiling, the whole of the glucina is precipitated in the form of a salt containing a great excess of base. The neutral nitrate, formate, chloride, bromide, and iodide of glucinum may be almost wholly converted into tribasic salts by digestion with hydrate of glucinum. The neutral nitrate may also be converted into the tribasic salt by partial neutralisation of the acid with ammonia: the sulphate also in like manner, but the solution does not bear dilution. The solution of the acetate dissolves hydrate of glucinum, till it is converted into a sexbasic salt.

**GLUCINUM, ALLOYS OF.** But little is known of the alloys of glucinum. An alloy of this metal with iron is obtained by heating glucina to whiteness in contact with iron and charcoal (Stromeyer), or with iron and potassium (H. Davy); also by decomposing glucina, in an atmosphere of hydrogen, by the current of a powerful voltaic battery, the negative pole of which is formed of an iron wire, which is fused by the current (H. Davy). The alloy obtained by Stromeyer is white and less malleable than iron, and dissolves in acids, forming a glucinum-salt and a ferrous salt.

**GLUCINUM, BROMIDE OF.**  $GBr$  or  $Be^*Br^*$ .—Glucinum takes fire when heated in bromine-vapour, forming a bromide, which sublimes in long colourless prisms, is fusible, volatile, and dissolves in water, with great rise of temperature. — Hydrate of glucina dissolves in aqueous hydrobromic acid, and the solution, when evaporated, yields deliquescent crystals of a hydrated bromide, which when ignited leave a residue of glucina. (Berthelot.)

**GLUCINUM, CHLORIDE OF.**  $GCl$ , or  $Be^*Cl^*$ .—Formed by heating the metal in chlorine or in hydrochloric acid gas, and by the action of aqueous hydrochloric acid on the metal or its oxide. The anhydrous chloride is prepared by passing dry chlorine gas over an ignited mixture of glucina or pulverised beryl with charcoal. It then collects in the colder parts of the tube, or in the receiver, in silky needles and flakes, thickly interwoven or caked together into a dense mass. It melts at a gentle heat, and at a higher temperature again sublimes in needles. It is less volatile than chloride of aluminium. Heated with potassium or sodium, it yields glucinum.

Chloride of glucinum dissolves in water, with considerable rise of temperature and a hissing noise; it is very deliquescent. The solution, which may also be obtained by dissolving glucina, or the metal, in hydrochloric acid, deposits on evaporation a crystalline mass, consisting of the hydrated chloride,  $GCl.H^2O$ . A *basic chloride*, or *oxychloride*, is obtained by boiling the aqueous solution with glucina, or by treating it with a quantity of ammonia not sufficient for complete precipitation.

**GLUCINUM, DETECTION AND ESTIMATION OF.** 1. *Reactions.*—Glucinum is not precipitated from neutral or acid solutions by *sulphydric acid*.

*Alkaline sulphides* throw down hydrate of glucinum as a bulky white precipitate, with evolution of *sulphydric acid*.

*Caustic potash* and *soda* form a gelatinous precipitate of hydrate of glucinum, soluble in excess of the alkali, but completely precipitated on boiling, if the solution is dilute, and redissolving only to a very slight extent on cooling; if the caustic alkali-solution was very concentrated, the hydrate does not separate from the boiling solution till water is added, but the precipitation then takes place immediately.

*Ammonia* also precipitates the hydrate, even in presence of ammoniacal salts; the precipitate is not soluble in excess of ammonia.

The *alkaline earths*, and likewise *magnesia* and *yttria*, precipitate glucinum as a hydrate. The *normal and acid carbonates of potassium and sodium* throw down a bulky precipitate of carbonate of glucinum, soluble in a large excess of the reagent. *Carbonate of ammonium* produces a similar precipitate, but soluble in a much smaller excess.

*Carbonate of barium* precipitates glucina completely at the boiling heat; in the cold, according to H. Rose (Handb. d. Chem. Anal. ii. 61), no precipitate is formed; but according to Awdziejew (Pogg. Ann. lvi. 101) and Weeren (*ibid.* xcii. 91), partial precipitation takes place. *Ordinary phosphate of sodium* throws down a flocculent precipitate. *Ferrocyanide of potassium* produces no precipitate at first, but the liquid becomes gelatinous after a while. *Alkaline succinates* form a white precipitate; *tincture of galls* throws down yellow flakes. Glucinum salts are not precipitated by sulphate of potassium, hydrofluosilicic acid, carbonate of calcium, oxalic acid, alkaline oxalates or tartrates, or by ferricyanide of potassium.

The reactions of glucinum are in most respects similar to those of aluminium. A sufficient distinction between the two is, however, afforded by the reaction with *carbonate of ammonium*, which dissolves the precipitates of glucinum formed by alkalis and alkaline carbonates, but not the corresponding precipitates of aluminium. A further distinction is that glucinum-compounds, moistened with nitrate of cobalt and heated before the blowpipe, do not give the blue colour which is characteristic of aluminium-compounds.

2. *Quantitative Estimation and Separation.*—Glucinum is precipitated from its solutions for quantitative estimation by ammonia, or better by sulphide of ammonium. The precipitate, when washed and ignited, yields pure anhydrous glucina.

The methods of separating glucinum from other metals are for the most part the same as those for the separation of aluminium.

When glucinum and aluminium occur together in solution, the best mode of separating them is that given by Berzelius, viz. to boil the precipitated hydrates with a highly concentrated solution of sal-ammoniac as long as ammonia continues to escape. The whole of the glucina then dissolves, and the alumina remains behind. To ensure complete separation, it is necessary to add the sal-ammoniac solution before precipitating, and continue the boiling for a considerable time, renewing the water as it evaporates, to prevent the solution becoming too concentrated. When the evolution of ammonia ceases, the solution is to be diluted with a large quantity of hot water, then filtered hot, and the glucina precipitated by sulphide of ammonium. The method

usually given for effecting this separation—viz. by digestion in a cold strong solution of carbonate of ammonium—is not satisfactory, because a portion of the alumina dissolves together with the glucina, although by itself it is quite insoluble in carbonate of ammonium. Neither does precipitation with carbonate of barium give satisfactory results, a portion of the glucina always going down with the alumina. (Weeren.)

According to V. Hofmeister, on the contrary (*J. pr. Chem.* lxxvi. 1), the method of digestion in carbonate of ammonia is the best of all methods of separating glucina from alumina, provided it be carried out as follows:—The mixture of the two earths precipitated by caustic ammonium and washed, is digested in a quantity of solution of carbonate of ammonium not much more than sufficient to dissolve the whole of the glucina, this quantity having been approximately determined beforehand. The alumina which remains is then perfectly free from glucina. The solution contains the whole of the glucina, together with a certain quantity of alumina; if the quantity of alumina thus dissolved is rather large, the solution becomes spontaneously turbid, after standing for 6 to 12 hours. The solution is acidulated with hydrochloric acid, heated till all the carbonic acid is expelled, and precipitated by caustic ammonia. The well-washed precipitate, if treated with a quantity of carbonate of ammonium smaller than that previously used, yields a residue of alumina, which may contain glucina; and in that case the resulting solution is free from alumina. The same treatment is now to be applied to this undissolved residue (or to the solution, if the residue is free from glucina); and in this manner a complete separation of the two earths is effected. The best way of precipitating the glucina from its solution in carbonate of ammonium is to supersaturate with hydrochloric acid, and then with ammonia mixed with a little sulphide of ammonium. (See also Scheffer, p. 853.)

3. *Atomic weight of Glucinum.*—The atomic weight of glucinum has not yet been determined with the same degree of accuracy as those of most other metals. The early determinations, founded on analyses of the chloride and sulphate, were much too high, the error having apparently arisen from the formation of basic salts in the precipitations, so that the separation of the base and acid was not complete.

Awdajew (*Pogg. Ann.* lvi. 101) found in chloride of glucinum prepared by the action of chlorine on a mixture of glucina and charcoal, from 86.7 to 88.3 per cent. of chlorine; whence, for the formula  $GCl_2$ , he finds  $G = 4.82$ , and for  $BeCl_2$ ,  $Be = 7.3$ .

From the analysis of the sulphate of glucinum,  $GSO_4$ , Awdajew found for the atomic weight of glucinum ( $S = 32.2$ ) values ranging from 4.665 to 4.722, mean  $G = 4.65$ , which, if reduced to the value which it should have for  $S = 32$ , becomes  $G = 4.62$ , or  $Be = 6.93$ .

From these determinations, the atomic weight of glucinum may be estimated approximately as  $G = 4.7$  or  $Be = 7$ .

**GLUCINUM, FLUORIDE OF.**  $GF$  or  $BeF^3$ .—The anhydrous fluoride is not known. The solution of hydrate of glucinum in aqueous hydrofluoric acid dries up to a colourless, transparent, gummy mass, which remains clear at  $60^\circ C.$ , but gives off water and becomes milk-white at  $100^\circ$ , then swells up, and at a red heat gives off part of its acid, provided the whole of the water has not previously been driven off. It dissolves readily in water, even after it has been heated. (Berzelius.)

*Fluoride of Glucinum and Potassium.*  $KFGF$ , or  $3KF.Be^2F^3$ .—Precipitated in small scaly crystals on mixing the solutions of the component fluorides. If the fluoride of potassium be added in excess to the solution of chloride of glucinum, the compound separates in the form of a jelly, but its solution in hot water yields crystalline scales on cooling. (Berzelius.)

**GLUCINUM, IODIDE OF.**  $GI$  or  $BeI^2$ .—Glucinum takes fire when heated in iodine vapour, the iodide subliming in colourless prisms easily soluble in water (Wöhler). It is less volatile than the chloride, and is decomposed by oxygen, even at the heat of a spirit-lamp, yielding iodine and glucina. (Debray.)

**GLUCINUM, OXIDE OF.** *Glucina, Beryllia, Beryllide, Säuerde.*  $G^2O$ , or  $Be^2O^3$ .—Glucina may be prepared from beryl or either of the other silicates of glucinum by calcination with alkaline hydrate or carbonate, or with quicklime. Weeren fuses an intimate mixture of 1 pt. finely pounded beryl and 3 or 4 pts. carbonate of potassium in a bessian crucible, keeping the mixture at a full white heat for two hours; treats the fused mass with hydrochloric acid in the usual way, to separate silica; precipitates the glucina, alumina, and ferric oxide with ammonia; and boils the precipitate with a strong solution of sal-ammoniac as long as ammonia continues to escape, frequently renewing the water. By this means the glucina alone is dissolved, and may be precipitated by ammonia or sulphide of ammonium.

Debray prepares glucina from the emerald of Limoges by the following process. The mineral, finely pounded (levigation with water is quite superfluous), is fused with half its weight of quicklime in an air-furnace, and the glass thus obtained is treated, first with



dilute, and then with strong nitric acid, till it is reduced to a homogeneous jelly. The product is then evaporated to dryness, and heated sufficiently to decompose the nitrates of aluminium, glucinum, and iron, and a small portion of the nitrate of calcium; and the residue, consisting of silica, alumina, glucina, sesquioxide of iron, nitrate of calcium, and a small quantity of free lime, is boiled with water containing sal-ammoniac, which dissolves the nitrate of calcium immediately, and the free lime after a while, with evolution of ammonia (if no ammonia is evolved, the calcination has not been carried far enough, and must be repeated). The liquid is then decanted; the precipitate, after thorough washing, treated with boiling nitric acid; and the resulting solution of alumina, glucina, and iron poured into a solution of carbonate of ammonium mixed with free ammonia. The earths are thereby precipitated without evolution of carbonic acid, and the glucina redissolves, after seven or eight days, in the excess of carbonate of ammonium. As the carbonate of ammonium may also dissolve a small quantity of iron, it should be mixed with a little sulphide of ammonium to precipitate the iron completely. Lastly, the carbonate of ammonium is distilled off, and the carbonate of glucinum which remains yields pure glucina by calcination.

According to G. Scheffer (*Ann. Ch. Pharm.* cix. 144), the preceding processes are attended with considerable loss of glucina: the following gives better results. A mixture of 7 pts. beryl and 13 pts. fluorspar is digested at  $100^{\circ}$ — $200^{\circ}$  C. with about 18 pts. sulphuric acid, in a leaden capsule (or in a porcelain capsule, especially if a somewhat smaller quantity of fluorspar be used), a large quantity of fluoride of silicon being thereby evolved. The mass is then heated nearly to redness in a capacious porcelain crucible, and dissolved in water acidulated with sulphuric acid, and the solution is mixed with 1.7 pts. sulphate of ammonium, or an equivalent quantity of sulphate of potassium, and left to itself till the greater part of the alumina contained in it has crystallised out in the form of alum. To separate the alumina still remaining in solution from the glucina, the liquid decanted from the alum-crystals is diluted with 6 or 8 times its volume of water, and digested for two or three days with granulated zinc, then heated with the zinc and filtered. The whole of the alumina is thereby precipitated as basic sulphate, while the glucina remains in solution, also as basic sulphate ( $G^2O.G^2SO^4$ ) together with sulphate of zinc. The greater part of the latter may be crystallised out as zinco-potassic sulphate by addition of sulphate of potassium (1.4 pts. of that salt to 1 pt. of zinc dissolved); the decanted liquid mixed with excess of acetate of sodium; the remaining zinc precipitated by sulphydric acid; the filtrate neutralised with ammonia; and the whole of the glucina precipitated by sulphide of ammonium. Common beryl treated by this process yields from 11 to 12.5 per cent. pure glucina.

Glucina is a soft, light, very bulky white powder, of specific gravity 2.967. It is tasteless and adheres to the tongue. It is not hardened by heat like alumina, but merely rendered less soluble in acids. When very strongly heated, it volatilises, like magnesia, without fusing. Ebelmen has obtained it in hexagonal prisms by exposing a solution of glucina in fused boracic acid to a powerful and long-continued heat. It may be more easily obtained in microscopic crystals, apparently of the same form, by decomposing the sulphate at a high temperature in presence of sulphate of potassium, also by calcining the double carbonate of glucinum and ammonium.

**Hydrate.**  $GHO$  or  $G^2O.H^2O$ .—This is the precipitate formed in glucinum-salts by caustic alkalis. It resembles trihydrate of aluminium when moist, but forms a powder when dry. It parts with its water at a high temperature, but without becoming incandescent. It dissolves in caustic potash and soda like alumina, but is precipitated by boiling, when the solution is diluted to a certain extent with water. According to Weeren, it dissolves slightly in ammonia, unless chloride or sulphide of ammonium is present. It absorbs carbonic acid from the air, in the dry, as well as in the moist state.

**GLUCINUM, OXYGEN-SALTS OF.** See p. 849; also the several Acids.

**GLUCINUM, PHOSPHIDE OF.** Glucinum burns in vapour of phosphorus, forming a grey powder, which is decomposed by water, with evolution of spontaneously inflammable phosphoretted hydrogen gas.

**GLUCINUM, SELENIDE OF.** Produced, with vivid incandescence, when glucinum is fused with selenium. It forms a crystalline brittle mass, grey on the fractured surface; is slowly dissolved and decomposed by water; but oxidises quickly, with separation of selenium, in contact with the air.

The precipitate formed by selenide of ammonium in solutions of glucinum-salts is probably impure hydrate of glucinum containing selenium.

**GLUCINUM, SULPHIDE OF.** Formed, with vivid incandescence, when glucinum is ignited in sulphur vapour; it is not produced by igniting glucina in

vapour of sulphide of carbon. It is a grey unfused mass, which dissolves slowly in water, without evolution of sulphuric acid, and is easily decomposed by acids, sulphuric acid being then evolved.

**GLUCINUM, TELLURIDE OF.** Produced, without emission of light, when glucinum is heated with tellurium; it is a grey powder, which decomposes gradually in contact with the air, and immediately in contact with water, giving off tellurhydric acid.

**GLUCOSAN.**  $C^6H^{10}O^5$ .—The anhydride of dextroglucose. Dextroglucose dried between  $100^\circ$  and  $110^\circ$  C. gives off water at  $170^\circ$ , becoming coloured at the same time, and is converted into glucosan, mixed, however, with small quantities of caramel and unaltered glucose, the latter removable by yeast, the former by charcoal. Glucosan is a colourless mass, scarcely sweet to the taste. It turns the plane of polarisation to the right, somewhat less strongly than dextro-glucose. It does not ferment immediately in contact with yeast, but only after being treated with dilute acids, which convert it into glucose. (Géllis, Compt. rend. li. 331.)

Glucosan may be regarded as a hexatomic alcohol, containing the tetratomic radicle  $C^6H^4$ , and represented by the formula  $\left\{ \begin{smallmatrix} (C^6H^4)^{10} \\ H^4 \end{smallmatrix} \right\} O^5$ ; in fact, by treating glucose with acids and with alcohol, compound ethers are obtained, related to glucosan in the same manner as the mannitanides and dulcitanides (p. 521) are related to mannitan and dulcitan. (Berthelot, Ann. Ch. Phys. [3] lx. 96 *et seq.*)

**Aceto-glucosan.**  $C^8H^{12}O^{11} = \left\{ \begin{smallmatrix} (C^6H^4)^{10} \\ (C^2H^2O)^2 \end{smallmatrix} \right\} O^5 = C^6H^{10}O^5 + 6C^2H^4O^2 - 6H^2O$ , *Glucose acétique, Hexacetoglucose*.—Obtained by heating glacial acetic acid with dextro-glucose or with cane-sugar to  $100^\circ$  C. for fifty hours; purified like the corresponding butyric compound. Trehalose and starch at  $180^\circ$  C., and dextrin at  $100^\circ$ , form with acetic acid, compounds similar to or identical with this.

Aceto-glucosan is a pale yellow or colourless neutral oil, having a bitter taste and faint odour. It dissolves abundantly in water, but not in all proportions, and is precipitated from the solution by chloride of calcium. It is soluble in alcohol and ether (Berthelot). It becomes acid in contact with the air, turns brown when heated, and burns with an odour of caramel. It is carbonised by oil of vitriol; slowly decomposed by boiling with dilute sulphuric acid, into acetic acid and dextro-glucose, which is further partly resolved into humous substances. With alcoholic hydrochloric acid, it forms acetate of ethyl and dextroglucose. Aceto-glucosan reduces potassio-cupric tartrate.

**Benzo-glucosan.**  $C^{10}H^{16}O^7 = \left\{ \begin{smallmatrix} (C^6H^4)^{10} \\ (C^2H^2O)^2 \end{smallmatrix} \right\} O^5 = C^6H^{10}O^5 + 2C^2H^4O^2 - 2H^2O$ , *Glucose benzoïque ou dibenzoïque, Dibenzoyl-glucose*.—Obtained by heating benzoic acid with dextro-glucose or cane-sugar to  $100^\circ$  C. for fifty hours, and purified like butyro-glucosan. The same or a similar compound is produced by heating benzoic acid with trehalose to  $180^\circ$ , or with cotton to  $200^\circ$ ; also at ordinary temperatures in a mixture of cotton, oil of vitriol, and benzoic acid; in all cases, however, only in small quantity.

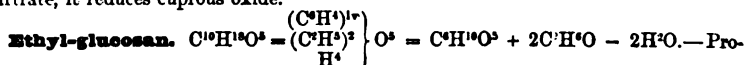
It is a neutral, semi-fluid oil, which produces grease-spots on paper, and has a bitter, pungent taste. It dissolves sparingly in water, easily in alcohol and ether. It burns with an odour of caramel when heated; is carbonised by oil of vitriol. With alcoholic hydrochloric acid, at a moderate heat, it yields benzoate of ethyl and dextro-glucose. It reduces potassio-cupric tartrate.

**Butyro-glucosan.**  $C^{14}H^{22}O^9 = \left\{ \begin{smallmatrix} (C^6H^4)^{10} \\ (C^2H^2O)^2 \end{smallmatrix} \right\} O^5 = C^6H^{10}O^5 + 2C^2H^4O^2 - 2H^2O$ , *Glucose butyrique, Dibutyryl-glucose*.—This compound is produced from cane-sugar, dextro-glucose, or trehalose, and in small quantity from dextrin, by heating with butyric acid.

Traces of the same or a similar compound are obtained when cotton or paper is heated with oil of vitriol and butyric acid. To prepare it, butyric acid is heated with cane-sugar or anhydrous dextro-glucose to  $100^\circ$  C. for fifty or sixty hours; the mass is exhausted with alcohol, and the solution filtered and evaporated. The residue is mixed with concentrated aqueous carbonate of potassium, a lump of caustic potash being added to neutralise it completely; the mixture is shaken up with ether; the ethereal layer is decolorised with animal charcoal; and the filtrate is evaporated over the water-bath.

Butyroglucosan is a pale yellow, viscid oil which produces grease-spots on paper. It is neutral, very bitter, with a slightly aromatic odour; retains water obstinately. It dissolves sparingly in water, easily in alcohol and ether. It burns when heated, emitting an odour of caramel. It is carbonised by oil of vitriol, and resolved, by heat-

ing with dilute sulphuric acid, into butyric acid and dextro-glucose. With alcoholic hydrochloric acid it yields dextro-glucose and butyrate of ethyl. From potassio-cupric tartrate, it reduces cuprous oxide.



duced when a mixture of cane-sugar, bromide of ethyl, and hydrate of potassium is heated in a sealed tube to 100° C. for several days, and the product, when cold, is treated with ether; ethyl-glucosan is thereby dissolved, and may be obtained by evaporation as a colourless oil. It has a bitter taste and a faint, agreeable odour, and is not volatile. It is nearly insoluble in water. From the ethereal solution it is almost completely precipitated by animal charcoal (Berthelot). By heating with dilute sulphuric acid, it is resolved into alcohol and dextro-glucose. From potassio-cupric tartrate it reduces cuprous oxide.

*Glucosotartaric acid*,  $\text{C}^{\text{H}^{\text{H}}}\text{H}^{\text{H}}\text{O}^{\text{H}}$  (p. 872), may be represented by the formula  $3 \left( \begin{array}{c} (\text{C}^{\text{H}^{\text{H}}})^{\text{H}} \\ (\text{C}^{\text{H}^{\text{H}}}\text{O}^{\text{H}})^{\text{H}} \end{array} \right) \text{O}^{\text{H}} \cdot \text{C}^{\text{H}^{\text{H}}}\text{O}^{\text{H}} \cdot 2\text{H}^{\text{H}}\text{O}$ , and *Glucosocitric acid*,  $\text{C}^{\text{H}^{\text{H}}}\text{H}^{\text{H}}\text{O}^{\text{H}}$ , by the formula  $2 \left( \begin{array}{c} (\text{C}^{\text{H}^{\text{H}}})^{\text{H}} \\ (\text{C}^{\text{H}^{\text{H}}}\text{O}^{\text{H}})^{\text{H}} \end{array} \right) \text{O}^{\text{H}} \cdot 4\text{C}^{\text{H}^{\text{H}}}\text{O}^{\text{H}} \cdot 5\text{H}^{\text{H}}\text{O}$ .

**GLUCOSE.**  $\text{C}^{\text{H}^{\text{H}}}\text{H}^{\text{H}}\text{O}^{\text{H}}$  or  $\text{C}^{\text{H}^{\text{H}}}\text{H}^{\text{H}}\text{O}^{\text{H}}$ .—A species of sugar produced, by the action of acids, certain ferments, and other reagents, and by processes going on in living plants, from cane-sugar, dextrin, starch, cellulose, and other carbohydrates; also by the decomposition of glucosides (p. 866); also by certain transformations of mannite and glycerin, and by the action of sodium-amalgam on oxalate of ethyl. There are two varieties of it, distinguished by their action on polarised light, viz. dextroglucose, which turns the plane of polarisation to the right; and lævoglucose, which turns it to the left.

**Dextroglucose.** *Ordinary glucose, Granular sugar (Krümelzucker)*, and, according to its origin, *Grape-sugar, Fruit-sugar, Honey-sugar, Starch-sugar, Diabetic sugar, Sugar of Urine, Chestnut-sugar, Rag-sugar*, some of which names are also used to denote glucose in general. It was first recognised as a distinct substance by Lowitz (Crell. Ann. 1792), and Proust (J. Phys. lxiii. 257); first prepared from starch by Kirchhoff (Schw. J. xiv. 389); from linen by Braconnot (Ann. Ch. Phys. [2] xii. 181). Its combinations with bases have been investigated chiefly by Peligot (*ibid.* lxvii. 136); those with organic acids by Berthelot (*ibid.* [3] liv. 74, lx. 95), who has likewise investigated its fermentation in contact with chalk and cheese (*ibid.* l. 322), and its formation from mannite and glycerin (*ibid.* l. 369). Our knowledge of glucose has been further extended by Dubrunfaut (Ann. Ch. Phys. [2] liii. 73; [3] xxi. 169, 178; Compt. rend. xxiii. 38; xxv. 308; xxix. 51; xxxii. 249; xlii. 228 and 739), who has eliminated much that does not properly belong to it, and more exactly characterised its properties.

*Occurrence.* a. *In the Mineral kingdom.*—Impressions of ferns from the clay-slate of Petit-œur, in Savoy, contain a sweet substance, which smells like caramel when burnt on charcoal, and perhaps consists of glucose (Calloud, Compt. rend. xxxiii. 544). On the alleged occurrence of sugar or dextrin in vegetable mould see Verdeil and Risler, Compt. rend. xxxv. 97, and the counter-statement of Petzholdt (J. pr. Chim. lx. 368.)

b. *In the Vegetable kingdom.*—Dextroglucose occurs abundantly in sweet fruits, frequently together with cane-sugar, and always with such a quantity of lævorotatory fruit-sugar that the mixture exhibits lævorotatory power, and is thence called inverted sugar (p. 863). The isolated occurrence of dextroglucose has been observed only in the following cases:—

A thick viscid liquid which, in the summer of 1842, covered the upper surface of the leaves of lime-trees, and at certain times of the day fell down like rain, contained cane-sugar and dextroglucose (Biot, Ann. Ch. Phys. [3] vii. 337; Langlois, *ibid.* vii. 348). Dextroglucose is contained in the manna of the ash-tree; a false manna, of unknown origin, was found to contain a peculiar sugar not invertible by acids, and having a molecular rotatory power equal to  $\frac{2}{3}$  of that of cane-sugar; perhaps maltose (Biot, Compt. rend. xiv. 49). Whether the sugar occurring in many other parts of plants should be considered as dextroglucose, is not yet decided. According to Buignet's researches (p. 712), cane-sugar and inverted sugar (which may be regarded as a peculiar substance, at least with reference to its origin), appear to be the most widely diffused; and the imperfectly investigated granular sugar (*Krümelzucker*) of many chemists appears to be inverted sugar, formed either in the plant, or during the process to which it is subjected for the extraction of the sugar.



*In Honey.*—This substance contains cane-sugar (which is gradually inverted by keeping), inverted sugar, and an excess of dextroglucose. (Dubrunfaut, *Compt. rend.* xxix. 51.)

*c. In the Animal body.*—In many animal liquids and tissues; in the liver, in the amniotic and allantoic liquids, in the blood, in the chyle, in the transudates, in the yolk and white of hens' eggs. In large quantity, to the amount of 8 or 10 per cent., in diabetic urine; in small quantity also in the urine of healthy men (Brücke; Bence Jones, *Chem. Soc. Qu. J.* xiv. 22). The urine of a fox fed exclusively on meat contained glucose (Vintschgau, *Wien. Akad. Ber.* xlii. 523). Compounds of glucose are likewise found in the animal body. (See GLUCOSIDES.)

*Formation.*—Of dextroglucose and fermentable sugars in general isomeric therewith, in so far as they cannot with certainty be referred to other species.

A. *By the transformation of Carbo-hydrates, with assumption of Water.* 1. Glucosan,  $C^6H^{10}O^5$  (p. 853), is converted into dextroglucose by boiling with dilute acids. (Gélis.)

2. Dextrin is converted into dextroglucose by boiling with dilute acids (Biot and Persoz). Diastase acts in like manner, according to Payen and Persoz; according to Musculus, it does not.—3. Under the same circumstances, soluble starch and common starch are converted into dextroglucose, after they have been previously converted wholly or partially into dextrin or other intermediate products. Dextroglucose is also formed from starch by continued boiling with water, by prolonged contact with glutin, saliva, animal gelatin, the pancreatic juice, the substance of the kidneys, mucous membrane, urine, bile, semen, blood-serum; and by watery infusions, prepared at  $40^\circ C$ , from the heart, brain, lungs, liver, kidneys, spleen, and muscles. (See *Gmelin's Handbuch*, viii. [2] 21.)

4. Glycogen is converted into dextroglucose under the same circumstances as starch.

5. In like manner, lichenin and paranylone are converted into glucose by boiling with acids.

6. Cellulose treated with strong sulphuric or hydrochloric acid (i. 819), or a concentrated aqueous solution of chloride of zinc, yields products which are converted into glucose when their aqueous solution is boiled with water. Glucose is likewise produced in the decomposition of lignosulphate of lead, and by the action of alkalis on pyroxyls. But it is doubtful also whether this sugar should be regarded as dextroglucose. According to Béchamp (*Ann. Ch. Phys.* [3] xlviii. 502), it yields, when treated with alcohol, two sorts of crystals, one having the hardness of cane-sugar, the others resembling dextroglucose.

The skin of the silk-worm, and that which remains in the cocoons when the butterflies escape, are capable of yielding a substance isomeric with cellulose, which may be converted into glucose. When the caterpillars are boiled for several hours with strong hydrochloric acid, and this treatment is repeated three times with the residue, and this residue is washed with strong potash-ley, then with water, and dried between  $100^\circ$  and  $110^\circ C$ , a white light substance nearly free from nitrogen is obtained, which gradually diffuses in oil of vitriol, forming a colourless gummy liquid. This solution, added by small quantities to boiling water, and boiled for an hour or two, yields fermentable sugar, which reacts, like glucose, with common salt and potassio-cupric tartrate. (De Luca, *Compt. rend.* liii. 102.)

7. Tunicin is decomposed by sulphuric acid, under the same circumstances as cellulose, into dextroglucose and a second substance.

8. Maltose, melezitose, trehalose and mycose, are completely converted into dextroglucose by boiling with dilute acids.

B. Another class of compounds yield by their decomposition dextroglucose and another product. This latter body is either isomeric with glucose; thus melitose is resolved, by dilute acids, yeast, and other bodies, into dextroglucose and eucalin; cane-sugar into dextro- and lævoglucose;—or it belongs to the class of non-saccharine bodies, in which case the compound which yields this second product and dextroglucose belongs to the class of Glucosides (p. 866).

C. In the decomposition of dulcite ( $C^6H^{10}O^6$ ) by nitric acid, there is formed, amongst other products, a sugar,  $C^6H^{12}O^6$ , which reacts with alkalis, potassio-cupric tartrate, basic nitrate of bismuth, and indigo, in the same manner as dextroglucose. (Carlet, *Compt. rend.* li. 137.)

D. *From Oxalate of Ethyl.*—When this compound is brought in contact with sodium-amalgam at low temperatures, and the product is agitated with ether, a solution is obtained from which a greasy mass separates on addition of water. This mass is a mixture of oxalate of sodium, another sodium-salt, and fermentable sugar. (Löwig, *J. pr. Chem.* lxxxiii. 133.)

E. *From Mannite or Glycerin.*—When a moderately concentrated aqueous solution of mannite, dulcite, or glycerin, is left for some time in contact with the testicles of man, or of the horse, dog, or cock, a peculiar fermentable sugar is produced, the form-

ation of which likewise takes place in certain cases, when, instead of the testicle, albumin, casein, fibrin, gelatin, or the tissue of the kidneys or pancreas, is employed. (Berthelot, *Ann. Ch. Phys.* [3] 1. 369.)

When to a solution of mannite or glycerin in 10 pts. water there is added such a quantity of comminuted testicle that its dried substance amounts to  $\frac{1}{20}$  of the mannite, and the mixture, contained in an open flask, is exposed to diffused daylight between 10° and 20° C., the liquid, after an interval varying from a week to three months, is found to contain (without the occurrence of putrefaction, which, indeed, is incompatible with the success of the experiment) a substance which reduces cupric tartrate. The testicular tissue, if separated at this time from the liquid by decantation and thorough washing, then again introduced under similar circumstances into a solution of mannite or glycerin, produces therein, in the course of a few weeks, a considerable quantity of sugar. This sugar is formed, sometimes in extremely small, sometimes in larger, quantity, amounting to  $\frac{1}{10}$  of the mannite or glycerin, and is partly further altered during the operation. It is not formed by the substance of the testicle, inasmuch as this substance is recovered for the most part unaltered, and gives up to the liquid, chiefly salts and albuminous substances, amounting to less than the weight of the sugar. — The sugar is probably levo-rotatory. It is deliquescent, uncrystallisable, and cannot be separated from the glycerin. It is apt to alter during the evaporation of its solution, is turned brown by alkalis, easily fermented by yeast, and reduces potassio-cupric tartrate. It is very soluble in water, alcohol, and glycerin, and slightly precipitable by ammoniacal sugar of lead. (Berthelot.) On the formation of sugar in the muscles and lungs of the fetal calf, see *Gmelin's Handbuch*, viii. [2] 489.

*Preparation.*—1. *From the juice of various kinds of fruit, especially of Grapes.*—The juice is boiled and skimmed; the free acid is neutralised with chalk or marble; and the liquid is concentrated to one-half, clarified by deposition and decantation, or further with white of egg, and evaporated to a syrup, not too thick. From this the grape-sugar separates after some weeks, and is purified by repeated solution in water and crystallisation.

2. *From Honey.*—1. White granular honey is diffused in  $\frac{1}{2}$  pt. of cold strong alcohol, which dissolves the more soluble levoglucose, and leaves the dextroglucose for the most part undissolved; the solution is separated from the sediment after a few hours; the sediment strongly pressed; the residue again triturated with  $\frac{1}{10}$  pt. alcohol; again pressed, and the undissolved portion is purified by solution in water and crystallisation (Braconnot, *Bull. Pharm.* iii. 360.) A similar process is followed by Proust, also by Cavezzalli (*Scher. J.* vii. 714), and Trommsdorff (*N. Tr.* ix. 1, 287).—2. Siegle spreads granular honey on dry porous bricks, whereby the liquid portion is absorbed, leaving, after a few days, a granular residue, which is recrystallised from warm alcohol with help of animal charcoal (*J. pr. Chem.* lxi. 148). The dextroglucose obtained by either of these processes will be contaminated with cane-sugar, if the honey contained that substance.

3. *From Starch by the action of dilute Sulphuric acid.*—1 pt. of starch is boiled with 4 pts. water, and a quantity of oil of vitriol weighing from  $\frac{1}{100}$  to  $\frac{1}{10}$  as much as the starch, the liquid being stirred and the water continually renewed till the liquid is no longer precipitated by alcohol. To bring it to this state, the boiling must be continued for a longer time in proportion as less sulphuric acid has been used; with the above proportions, from 6 to 36 hours' boiling is required. The dextroglucose then contained in the solution is separated and purified in the same manner as that from grape-juice (Kirchhoff). In preparing starch-sugar on the large scale, the ebullition is produced by passing over-heated steam into the mixture contained in closed casks. When starch is boiled with water and 2 per cent. oil of vitriol, the liquid being evaporated after 5 or 7 hours, at which time it is no longer precipitated by alcohol, an uncrystallisable syrup is obtained. It is only after longer boiling that the whole of the dissolved matter is converted into dextroglucose, part of which moreover undergoes further alteration, so that the liquid does not easily yield crystals by evaporation (Anthon, *Dingl. pol. J.* cli. 218). After the sulphuric acid has been neutralised by chalk, a small quantity of acetic acid must be added before boiling the liquid, since an excess of lime leads to the formation of bitter products of decomposition. (*Polyt. Centr.* 1854, p. 252.)

4. *From Starch, by the action of Gluten, Malt, or Diastase.\**—2 pts. of starch well mixed by stirring with 4 pts. of cold water are diffused in 20 pts. of boiling water, and the paste thus formed is digested for eight hours at 50° to 70° C. with 1 pt. of dried and pulverised wheat-gluten. From the syrup obtained by evaporation, alcohol extracts the sugar, leaving the starch which is still but slightly altered, and the solution yields the sugar by evaporation.

\* The product thus obtained is perhaps not dextroglucose, but maltose (q. v.)



100 pts. of starch are suspended in 400 pts. of cold water; the mixture is poured into 2000 pts. of boiling water, and after the whole has cooled to  $65^{\circ}\text{C}$ ., 2 pts. of diastase dissolved in 20 pts. of cold water are added. The mass, which in a few minutes becomes perfectly fluid, is kept for 2½ hours at a temperature between  $60^{\circ}$  and  $65^{\circ}\text{C}$ .; evaporated as quickly as possible at  $60^{\circ}$ , or better in vacuo, to  $34^{\circ}\text{Bm}$ ., and left to itself for some days in shallow vessels. By treating the syrup, which is sometimes crystalline, with alcohol of 95 per cent., at a temperature of  $75^{\circ}\text{C}$ ., cooling the solution out of contact of air, filtering, reducing the filtrate to a syrup by distillation and concentration, and leaving the syrup to itself in vacuo, crystals are obtained which may be purified by pressure, renewed treatment with alcohol, and recrystallisation from 4 pts. water at  $65^{\circ}$ , with help of animal charcoal. The diastase may be economically replaced by 18 times the quantity of malt. (Guérin-Varry.)

5. *From Linen*.—(See i. 819.) To 12 pts. of linen purified as completely as possible by treatment, first with potash-ley, then with water, and dried, 17 pts. oil of vitriol are very slowly added, so that no heating may take place; the mass is kneaded together, left to itself for 24 hours, then dissolved in a very large quantity of water; the solution is boiled for 10 hours; the acid is saturated with chalk; the liquid is filtered and evaporated; and the glucose which separates after some days is purified by recrystallisation (Braconnot). Vogel uses sulphuric acid of sp. gr. 1.8, which blackens the linen less than the strongest acid, and leaves the mass to itself for two days.

6. *From the Urine of diabetic patients*.—The crystals obtained by evaporating the urine are pressed (after being separated from the chloride-of-sodium compound of glucose) and purified by crystallisation from boiling alcohol (Chevreul), or by digestion with cold alcohol and subsequent recrystallisation (Prout). Addition of ether to the alcoholic solution favours the crystallisation (Peligot, Hünefeld). The urine is evaporated to a syrup on the water-bath; the residue exhausted with alcohol; the tincture precipitated with basic acetate of lead; the lead separated from the filtrate by sulphuretted hydrogen; and the clear liquid evaporated to a syrup and allowed to stand till it deposits crystals (Hünefeld, J. pr. Chem. viii. 560). Frequently nothing but crystals of the chloride-of-sodium compound of glucose are obtained on evaporating diabetic urine. (Lehmann, *Gmelin's Handbook*, viii. [2] 568.)

*Properties*.—Dextroglucose separates from its aqueous solution by slow evaporation in white, opaque, granular, hemispherical or cauliflower-shaped masses, consisting of a hydrate  $\text{C}^6\text{H}^{12}\text{O}^6 \cdot \text{H}^2\text{O}$ ; but from alcohol of 95 per cent. or upwards, it separates in anhydrous, microscopic, sharply-defined needles, which melt at  $140^{\circ}\text{C}$ . to a colourless, transparent mass (O. Schmidt, *Dissertation über Traubenzucker*, Göttingen, 1861). These anhydrous crystals are, however, frequently mixed with small portions of the hydrate. Anhydrous glucose is also obtained as a white powder by heating the hydrate to  $55^{\circ}$  or  $60^{\circ}\text{C}$ . in a stream of dry air, and as a fused transparent mass by heating the hydrate to  $100^{\circ}$ .

Dextroglucose is much less soluble in water than cane-sugar, requiring for solution  $1\frac{1}{2}$  times its weight of cold water; in boiling water it dissolves in all proportions, forming a syrup which has a very sweet taste, but is not so ropy as the syrup of cane-sugar. Pulverised glucose placed on the tongue produces a pungent and mealy taste, becoming slightly saccharine as the substance dissolves. 2½ pts. glucose according to Prout, 2 pts. according to Dubrunfaut, sweeten as much as 1 pt. of cane-sugar.

The following table, calculated by Pohl (Wien. Akad. Ber. xi. 664), from determinations by Graham, Hofmann, and Redwood, exhibits the quantities of anhydrous glucose contained in aqueous solutions of different specific gravity:

Quantity of anhydrous glucose in 100 pts. solution.	Specific gravity of solution.	Quantity of anhydrous glucose in 100 pts. solution.	Specific gravity of solution.
2	1.0072	15	1.0616
5	1.0200	17	1.0693
7	1.0275	20	1.0831
10	1.0406	22	1.0909
12	1.0480	25	1.1021

Dextro-glucose is also less soluble than cane-sugar in alcohol: the solution, saturated at the boiling heat, deposits crystals which retain a portion of alcohol with considerable force.

The molecular rotatory power of anhydrous glucose ( $\text{C}^6\text{H}^{12}\text{O}^6$ ), for the transition-tint (see LIGHT, POLARISED), is  $[\alpha] = +53.2^{\circ}$  (Dubrunfaut),  $57.44^{\circ}$  (Béchamp),  $55.15^{\circ}$  (Pasteur); for the monohydrate ( $\text{C}^6\text{H}^{12}\text{O}^6 \cdot \text{H}^2\text{O}$ ),  $[\alpha] = +48^{\circ}$  (Dubrunfaut),  $53.03^{\circ}$  (Béchamp). A freshly prepared solution of hydrated glucose (also of the crystals of anhydrous glucose obtained from absolute alcohol, or of dehydrated glucose prepared without fusion) shows a rotatory power equal to twice the above; but it gradually sinks to this point and then remains constant; but if the glucose has been



dehydrated by fusion, its solution, even when freshly prepared, possesses the same rotatory power as that acquired by a solution of the crystals after long standing. Dubrunfaut distinguished the glucose contained in a freshly-prepared solution as *glucose birotatoire*. The solution of the crystals in wood-spirit retains its rotatory power for a longer time than the aqueous solution.

*Decompositions.*—1. When dextroglucose dried at 110° C. is heated to 170°, it gives off one at. water, and is converted into glucosan,  $C^6H^{10}O^5$  (Gélin, p. 854). When heated for a long time to 150°, it turns brown, and is then hygroscopic after cooling (O. Schmidt). Between 210° and 220° C., it swells up more than cane-sugar, gives off a larger quantity of water, and yields caramel (Peligot). The products formed at high temperatures are similar to those obtained from cane-sugar (i. 747), but are somewhat more fusible, more easily soluble in water, and less soluble in alcohol.

2. Glucose froths up in the open fire, evolves a smell of burned sugar, and burns away with flame.

3. When oxygen is passed over glucose mixed with spongy platinum, formation of water and carbonic anhydride commences between 140° and 150° C., and at 250° the glucose is completely decomposed (Reiset and Millon, Ann. Ch. Phys. [3] viii. 268). Aqueous glucose in contact with platinum-sponge does not absorb oxygen; but, if potash-ley is also added, it becomes heated, and is oxidised to carbonic anhydride and water (Döbereiner). It yields formic acid when heated with *chromic acid* and sulphuric acid, or with *peroxide of manganese* and sulphuric acid (Hünefeld). Aqueous glucose does not alter *acid chromate of potassium* when heated with it (Reich). By distilling 1 pt. glucose with 1 pt. oil of vitriol, 1 pt. peroxide of manganese, and 30 pts. water, a distillate is obtained which exhibits the reactions of aldehyde, and possesses also the smell of acrolein (Liebig). Glucose is not altered by boiling with peroxide of manganese alone (Stürenberg), neither is it altered by permanganate of potassium (Monier). It takes fire when triturated with 6 pts. *peroxide of lead* (Böttger). On adding small quantities of glucose to a boiling pulp of peroxide of lead and water, carbonate and formate of lead are obtained:  $C^6H^{12}O^6 + 8Pb^{2+}O^2 = 4CHPbO^2 + 2Pb^{2+}CO^2 + 4Pb^{2+}O + 4H^2O$ . (Stürenberg.)

4. Dextroglucose behaves like milk-sugar when its *aqueous solution* is heated, that is to say, it turns yellow, and finally dark brown, and, if afterwards left to evaporate, leaves an acid deliquescent syrup, which does not crystallise, even after several months (Hoppe, Chem. Centr., 1860, p. 64). The rotatory power of the aqueous solution does not alter by standing for ten months (Maumené, Compt. rend. xxxix. 916). A concentrated aqueous solution becomes yellow when heated in a chloride-of-sodium bath, but its rotatory power is scarcely altered in 40 to 80 hours. (Soubeiran.)

5. Its aqueous solution, mixed with 1 at. acid carbonate of potassium, and then with 1 at. *iodine*, and warmed, yields iodoform. (Millon.)

6. Heated in a sealed tube with *bromine* in presence of water, it yields hydrobromic acid, a dark-brown liquid, and humus-like products. (Barth and Hlasiwetz.)

7. *Chlorine* converts glucose into a brown or black mass containing caramelin, i. 748 (Maumené). *Stannic chloride* acts upon glucose in the same way as upon cane-sugar, converting it into Maumené's caramelin (i. 749).

8. Fuming *nitric acid* converts glucose into nitro-glucose (Flores Domonté and Ménard). When heated with common, or moderately diluted nitric acid, glucose yields saccharic acid (Heintz) and oxalic acid, but no tartaric acid. (Liebig.)

9. By heating glucose with syrupy aqueous *phosphoric acid* to 140°, a small quantity of a saccharide is obtained. (Berthelot.)

10. Glucose dissolves without coloration when triturated with cold oil of vitriol, forming glucoso-sulphuric acid. This reaction distinguishes glucose from cane-sugar, which is quickly blackened by oil of vitriol. It chars when gently heated with 4 pts. oil of vitriol, and evolves carbonic oxide and carbonic anhydride (Filhol). When glucose is boiled with dilute sulphuric acid, the liquid becomes brown and yields a deposit of ulmin and ulmic acid; when air has access, formic acid is also produced. (Malaguti, Ann. Ch. Phys. liv. 417.)

11. Glucose long boiled with *hydrochloric acid* becomes unfermentable. (Bödeker.)

12. When heated with aqueous *iodic acid*, it is slowly decomposed into carbonic anhydride and water. (Millon.)

13. Mixed with water and an equal quantity of *arsenic acid*, and exposed to the sun, it becomes red or brown after three or four days. (Böttger.)

14. Honey behaves with *oxalic acid* in the same way as cane-sugar. (Döbereiner.)

15. The rotatory power of aqueous glucose is but very slightly altered by long heating in a chloride-of-sodium bath with *acetic acid*. (Soubeiran.)

16. By heating dextroglucose with *organic acids*, compounds are formed, with elimination of water, which belong to the class of *Saccharides*, and no longer possess the properties of the acid and of sugar, but are capable of breaking up again, by

assimilating water, into the acid and dextroglucose (Berthelot). See GLUCOSIDES and SACCHARIDES.

17. Gaseous ammonia passed over dextroglucose heated in a water-bath, or to  $110^{\circ}$ , is rapidly absorbed; water holding carbonate of ammonium in solution distilling over, while a brown tasteless nitrogenous residue is left. (P. Thénard, Rep. Chim. pure, 1861, p. 20.)

18. Glucose is decomposed by long contact with *alkalis, alkaline earths*, and some *metallic oxides*, forming glucic acid (Peligot). When it is heated with *potash-ley*, the solution becomes dark brown, evolves a smell of caramel, and contains, besides glucic acid, Peligot's melassic acid.

19. A thick syrup of glucose distilled with *lime* yields an oil from which metaceton and phorone can be obtained by fractional distillation. (Liè-Bodart, Ann. Ch. Pharm. c. 354.)

20. Aqueous glucose heated with *nitrate of barium* to  $180^{\circ}$  C. for 48 hours in a sealed tube, yields a body which is insoluble in water, and contains a small quantity of nitrogen, while an acid colourless solution remains, which quickly becomes coloured on exposure to the air, and contains neither nitric acid nor ammonia, but evolves a large quantity of ammonia when fused at a red heat with hydrate of barium. (P. Thénard, Bull. Soc. Chim., 1861, p. 61.)

21. By heating aqueous glucose with aqueous carbonate of sodium and *basic nitrate of bismuth*, a black-brown liquid and greyish-brown precipitate are obtained (Böttger, Jahrb. pr. Pharm. xxii. 29). Glucose can be detected in cane-sugar or in urine by this reaction. (Böttger, J. pr. Chem. lxx. 432.)

22. Crystallised glucose, evaporated with excess of *oxide of lead*, loses 11.14 per cent. (10.4 per cent. according to Guérin-Varry) of its weight, but the residue is brown, and smells of burnt sugar (Berzelius). A mixture of crystallised glucose with oxide of lead loses in weight 28 per cent. at  $110^{\circ}$  C., the sugar being converted into melassic acid. (Peligot.)

23. *Ferric sulphate* and *chloride* are reduced to ferrous salts by boiling with aqueous glucose (Hünefeld, J. pr. Chem. vii. 44). *Ferric hydrate* is reduced in the cold, still more easily on boiling (Kuhlmann, Compt. rend. xlix. 257). An aqueous mixture of 6 pts. tartaric acid, 240 pts. crystallised carbonate of sodium, and 5 or 6 pts. crystallised ferric chloride, if heated to boiling, filtered hot, and then mixed with glucose, becomes darker coloured, and deposits a precipitate containing ferrous oxide. (Löwenthal, J. pr. Chem. lxxiii. 71.)

24. A concentrated solution of glucose mixed with *nitrate of cobalt* and a small quantity of fused caustic potash, remains clear on boiling, or, if very concentrated, deposits a light-brown precipitate (Reich). The presence of glucose in a solution of cane-sugar prevents the production of the violet-blue precipitate, which solutions of pure cane-sugar give with solutions of cobalt and potash. (Reich, J. pr. Chem. xliii. 72.)

25. An aqueous solution of glucose mixed with *potash-ley*, and then with *cupric sulphate*, dissolves the cupric hydrate which separates at first, with a deep blue colour, and deposits cuprous oxide after some time in the cold, immediately if heated. The production of this precipitate makes it possible to detect and distinguish  $\frac{1}{100,000}$  pt. glucose from cane-sugar, starch, or gum; by the reddish coloration of the solution,  $\frac{1}{1,200,000}$  pt. glucose can be detected (Trommer, Ann. Ch. Pharm. xxxix. 361). Under the same conditions, 1 at. glucose reduces 5 at. cuprous oxide (formed from 10 at. cupric oxide) from a solution of cupric sulphate mixed with a sufficient quantity of tartaric acid and then with potash: a solution usually called *potassio-tartrate of copper*. A similar reduction takes place when *cupric acetate* is boiled with a solution of glucose; cuprous hydrate is then deposited, acetic acid is given off, and the solution retains a copper salt which has not yet been examined. Nitrate of copper is not reduced by glucose.

26. *Mercurous nitrate* is not altered by aqueous glucose at  $100^{\circ}$  C. (Baumann.)

27. Glucose throws down metallic silver from aqueous *nitrate of silver*, as a black precipitate, on boiling; from aqueous ammonio-nitrate of silver, as a dirty-grey precipitate (Baumann). Ammoniacal glucose throws down silver as a metallic mirror from aqueous silver-salts, in the cold or when heated (Liebig). The metal is also separated when a mixed solution of nitrate of silver and glucose is allowed to stand for 14 days (Schwertfeger, Jahrb. pr. Pharm. vii. 292). A solution of glucose, mixed with carbonate of sodium, or with potash-ley, reduces chloride of silver to the metallic state on boiling; it reduces carbonate of silver even at  $66^{\circ}$ — $70^{\circ}$  (Schiff, Ann. Ch. Pharm. cix. 68). On heating glucose with oxide of silver and potash-ley, oxalic acid is formed. (Liebig, *ibid.* cxiii. 12.)

28. Glucose is not changed by ebullition with aqueous *platinic chloride*. (Baumann.)

29. If solution of glucose mixed with *indigo*, or with solution of indigo, is boiled, and carbonate of sodium dropped in, the liquid is decolorised by the conversion of the indigo-blue into indigo-white. (E. Mulder, N. Br. Arch. xcv. 268.)

30. An aqueous solution of 1 pt. *ferricyanide of potassium (red prussiate)* mixed with  $\frac{1}{2}$  pt. hydrate of potassium, and heated to 60° or 80° C., is decolorised when aqueous glucose is dropped in. Inverted sugar behaves in the same way, but cane-sugar and dextrin prepared by roasting (the latter not even after being boiled for a short time with acids) do not decolorise the solution. 100 c.c. of a solution containing in that bulk 10.98 grms. ferricyanide and  $5\frac{1}{2}$  grms. hydrate of potassium, is decolorised by the inverted sugar formed from 1 grm. of cane sugar. (Gentele, Dingl. pol. J. clii. 68; Jahresb. d. Chem. 1859, 698.)

31. Dextroglucose is capable of undergoing *vinous fermentation* (p. 729). It is not thereby first converted into another kind of sugar, certainly not into lævoglucose; for the liquid has, at every stage of the process, a dextro-rotatory power proportional to the quantity of glucose contained in it, and yields crystals of dextroglucose by evaporation. (Ventzke, J. pr. Chem. xxv. 78; Mitscherlich, Pogg. Ann. lix. 94; Dubrunfaut, Ann. Chim. Phys. [3] xxi. 171.)

32. In the *lactous fermentation* (p. 630) of dextro-glucose, the rotatory power diminishes constantly in the proportion corresponding to the quantity of acid formed (Dubrunfaut). *Erythrozym* acts on glucose in the same way as upon sugar. (Schunck, J. pr. Chem. lxxiii. 222. See also p. 267.)

Left to itself in contact with *chalk*, or *cheese*, or *gelatin*, or other nitrogenous animal substances, at 40° C. for weeks or months, an aqueous solution of glucose is capable, according to Berthelot, of undergoing a decomposition, different from fermentation properly so called (which takes place under the influence of yeast), whereby the nitrogenous substance as well as the sugar suffers decomposition, and nitrogen, carbonic anhydride, and hydrogen, are evolved, while alcohol, and butyrate and lactate of calcium are formed. Yeast is not produced under these circumstances, unless air has excess to the liquid. In other cases, cells resembling yeast make their appearance without any alcohol being produced; so that, under these particular conditions, yeast and alcohol are independent of each other. The chalk may be replaced by many other carbonates—50 grms. glucose, 800 grms. water, 60 grms. chalk; and 20 grms. cheese, left to stand at the mean temperature, produced at first lactate of calcium, but after five months this had disappeared, and the liquid contained butyrate of calcium, and a quantity of alcohol amounting to 2 per cent. of the glucose used. Alcohol was also formed after addition of fatty oil, or of oil of turpentine, but there was no lactate of calcium; addition of sulphide of carbon prevented the destruction of the sugar. A mixture of 1 pt. glucose, 10 pts. water,  $\frac{1}{2}$  pt. cheese, and 1 pt. *magnesia alba* contained, after five months, alcohol, lactate, and a small quantity of butyrate of magnesium, the sugar being completely destroyed. In this and in some of the following cases, it remained doubtful whether or not yeast was formed. Similar products were formed when an equal quantity of carbonate of barium was used instead of the magnesia. Alcohol was obtained when the carbonate of zinc, manganese, iron, nickel, and lead, or peroxide of manganese, oxide of zinc, cupric oxide, metallic iron, and metallic zinc were used instead of the magnesia; with oxide of lead and carbonate of copper no alcohol was obtained. Alkaline carbonates, or borate, phosphate, or hyposulphite of sodium added in equal quantity, did not prevent the production of alcohol. By caustic soda, the sugar was destroyed without yielding alcohol; with sulphite of sodium or calcium, it remained unaltered. When the magnesia was replaced by carbonate of ammonium, alcohol was formed together with a peculiar acid, the calcium-salt of which was deliquescent, and contained at 110° C., 36.6 per cent. carbon, 5.2 hydrogen, and 18.9 lime, nearly corresponding to the formula  $C^9H^{14}Ca^2O^8$ . (Berthelot, Ann. Ch. Phys. [3] l. 351.)

33. When strong sulphuric acid is gradually added to aqueous solution of *ox-bile*, until the precipitate at first produced is re-dissolved, the liquid assumes, on addition of a small quantity of solution of glucose, a violet-red colour, similar to that of a solution of permanganate of potassium. Cane-sugar and starch also act in the same way (Pettenkofer, Ann. Ch. Pharm. lii. 90). According to Pettenkofer, this reaction is applicable to the detection of sugar in urine, and also in blood, after removal of albumin by boiling with alcohol. Many other protein-compounds, likewise oil-fat, oil of almonds, and many other oils, behave like bile (M. S. Schultze, Ann. Ch. Pharm. lxxi. 266). The extractive matter of healthy urine, employed in place of sugar, produces the same coloration, which may sometimes be obtained with *ox-bile*, sulphuric acid, and a small quantity of water only (Van den Broek, J. pr. Chem. xxxix. 362). According to Schunck (Phil. Mag. [4] xxiii. 179), the extractive matters in healthy urine yield, when decomposed in aqueous solution by means of strong acids, a sugar possessing the composition and some of the properties of glucose, but uncrystallised and insipid.



*Combinations of Dextroglucose.*

A. With Water.—Melted glucose deliquesces at first in the air by absorption of water (7.9 per cent. according to Guérin-Varry), and solidifies as soon as the quantity of water is sufficient for the formation of crystals, to a crystalline, granular mass. Glucose dried without being melted absorbs no water when exposed to the air (Béchamp, *Compt. rend.* xlii. 900).—The crystals of anhydrous glucose, obtained from alcohol, if dissolved in a small quantity of water and evaporated over oil of vitriol, are found to have taken up a quantity of water amounting to only 3.1 per cent. of their weight. Anhydrous glucose appears, therefore, capable of existing for some time in aqueous solution (O. Schmidt). An aqueous solution evaporated to a thin syrup solidifies after a few days to a granular mass; if evaporated to a thick syrup it does not solidify, owing to absence of sufficient water, until it has absorbed more water from the air.

a. *Hemi-hydrated glucose.* Anthon's *hard-crystallised glucose*.—Prepared on the manufacturing scale by a process which is kept secret. In the crystallised state, air-dried, it contains  $2\text{C}^6\text{H}^{12}\text{O}^6 \cdot \text{H}^2\text{O}$ , and does not diminish in weight when placed over oil of vitriol at  $13^\circ$ . (Anthon, *Chem. Centr.* 1859, p. 289.)

b. *Mono-hydrated glucose.* *Crystallised glucose.*  $\text{C}^6\text{H}^{12}\text{O}^6 \cdot \text{H}^2\text{O}$ . This hydrate is generally obtained in white, opaque, granular hemispherical or cauliflower-shaped masses, with occasional shining surfaces. The crystals are seen under a magnifying glass to be six-sided tables, whose lateral faces cut each other at angles of about  $120^\circ$ . Mitscherlich obtained on one occasion transparent well-formed crystals, as much as 0.6 millimetre long, which showed double refraction (Biot, *Compt. rend.* xxiii. 909).—The crystals are brittle and grate between the teeth. Specific gravity 1.3861. (Guérin.)

The mono-hydrate becomes soft at  $60^\circ\text{C}$ . more so still at  $65^\circ$ , losing a small quantity of water; at  $70^\circ$  it becomes doughy; at  $90^\circ$ – $100^\circ$ , it deliquesces to a thin syrup, and loses in all 9.8 per cent. water (Guérin-Varry). It melts between  $70^\circ$  and  $80^\circ$ ; if dried in vacuo, between  $90^\circ$  and  $100^\circ$  (Béchamp), at  $86^\circ$  (C. Schmidt) loses 9–9.1 per cent. water (3 at. = by calculation 9.09 per cent. water) (Peligot). In a stream of dry air it loses only hygroscopic water at  $50^\circ$ , but between  $55^\circ$  and  $60^\circ$  part of its water of crystallisation, and, if kept at this temperature for a few hours, it may be heated to  $80^\circ$  or  $100^\circ$  without melting. (Béchamp, *Compt. rend.* xlii. 898.)

B. With Metallic oxides. GLUCOSATES.—Dextroglucose unites with the alkalis, alkaline earths, and oxide of lead, forming compounds which may be regarded as glucose in which the hydrogen is more or less replaced by a metal. These compounds are more easily decomposed than the corresponding compounds of cane-sugar. An aqueous solution of glucose takes up a large quantity of baryta, strontia or lime, forming yellow solutions precipitable by alcohol, which, even when protected from the air, become darker and decomposed when kept or heated. Their taste is bitter and slightly alkaline, and when evaporated in vacuo, they leave transparent, brittle masses, sometimes containing unaltered glucose. Dextroglucose also forms definite compounds with bromide and chloride of sodium.

*Glucosates of Barium.*—a.  $\text{C}^6\text{H}^{11}\text{BaO}^6$ .—An alcoholic solution of hydrate of barium is added to excess of glucose dissolved in alcohol, and the precipitate is washed with strong alcohol and dried in vacuo over sulphuric acid. It is a nearly white, loose powder, having a caustic taste; easily soluble in water. (W. Mayer, *Ann. Chim. Pharm.* lxxxiii. 138.)

b.  $4\text{C}^6\text{H}^{11}\text{BaO}^6 \cdot \text{Ba}^2\text{O} + 6\text{aq.}$ —A solution of glucose in wood-spirit is mixed with a solution of baryta (not in excess) in aqueous wood-spirit; the precipitate is washed with wood-spirit and dried in vacuo, first over quicklime, then over oil of vitriol (Peligot). Soubeiran precipitated a mixture of baryta-water and excess of glucose with alcohol. The salt acquires a bright yellow colour at  $100^\circ\text{C}$ . in vacuo without undergoing further alteration; at a higher temperature it froths up and chars. (Peligot.)

*Glucosate of Calcium.*  $\text{C}^6\text{H}^{10}\text{CaO}^6 + \text{aq.}$ —A freshly prepared solution of hydrate of calcium in aqueous glucose is precipitated by alcohol (Peligot). Soubeiran agitates glucose with milk of lime, adds a small quantity of glucose to the filtrate to neutralise the excess of lime, and precipitates with alcohol. The salt does not become perfectly dry till it has stood a long time in vacuo. (Soubeiran.)

*Glucosates of Lead.*—a.  $\text{C}^6\text{H}^9\text{PbO}^6 + \text{aq.}$ —An ammoniacal solution of neutral acetate of lead is added to excess of glucose-solution till the precipitate becomes permanent. The white precipitate washed out of contact with carbonic acid and dried in vacuo, turns yellow at  $150^\circ\text{C}$ . without further alteration. (Peligot.)

b.  $\text{C}^6\text{H}^9\text{PbO}^6$ .—25 pts. aqueous ammonia are added to the mixed solution of 20 pts. dextroglucose (or inverted sugar, according to Soubeiran) and 35 pts. neutral acetate of lead in 400 pts. water, and the precipitate is dried, first in vacuo, then at  $100^\circ$ . (Soubeiran.)

*Glucosate of Bromide of Sodium,*  $2\text{C}^6\text{H}^{12}\text{O}^6 \cdot \text{NaBr}$ .—This compound, prepared by

leaving a solution of 1 at. bromide of sodium and 2 at. glucose to evaporate in a warm place, washing the crystals which separate with cold water, and recrystallising from alcohol, forms anhydrous rhombohedral crystals which are perhaps isomorphous with the following compound; when examined by polarised light they exhibit the characters of uniaxial crystals. (Stenhouse, Chem. Soc. J. xvi. 297.)

*Glucosates of Chloride of Sodium.*—*a.*  $2\text{C}^6\text{H}^{12}\text{O}^6\cdot\text{NaCl} + \text{aq.}$ —This compound, discovered by Calloud (J. Pharm. xi. 562), crystallises out when diabetic urine is evaporated, also from solutions containing 1 at. or less of chloride of sodium to 2 at. glucose; according to Brunner, from solutions of glucose saturated with chloride of sodium. When a layer of ether-alcohol is poured upon diabetic-urine syrup, and the whole allowed to stand quietly, transparent crystals of this compound are obtained (Hünefeld, J. pr. Chim. vii. 46). Glucose from diabetic urine yields this compound far more easily than glucose of different origin (Erdmann and Lehmann). It is purified by crystallisation from water at the common temperature. (Brunner.)

It forms transparent, colourless, lustrous crystals, attaining half an inch in length, and belonging, according to Kobell and Schabus, to the hexagonal system, and consisting of hexagonal prisms and rhombohedrons. According to Pasteur, on the other hand (Ann. Ch. Phys. [3] xxxii. 92), they belong to the dimetric or rhombic system, forming hemihedral rhombic prisms  $+ \frac{P}{2} - \frac{P}{2} \cdot \tilde{P} \infty$ , resembling double pyramids of the hexa-

gonal system, but having the angles at the base =  $120^\circ 12'$  and  $119^\circ 54'$ . On cutting a crystal into laminae with parallel faces perpendicular to the axis which joins the summits of the two six-sided pyramids, and sending a ray of polarised light through these laminae, they do not exhibit the optical properties which belong to crystals of the hexagonal system (Pasteur). For further details respecting the crystalline form, see *Gmelin's Handbook*, xv. 236.

The aqueous solutions, when freshly prepared, exhibit dextro-rotatory power corresponding to the quantity of glucose contained in it, viz. for the transition-tint,  $[\alpha] = 47.14^\circ$ ; but the rotatory power continually diminishes, especially if the solution is hot, just like that of a pure solution of glucose (p. 858).

*b.*  $\text{C}^6\text{H}^{12}\text{O}^6\cdot\text{NaCl} + \frac{1}{2} \text{aq.}$ —Calloud obtained from glucose and common salt crystals containing 25 per cent. chloride of sodium, the existence of which was afterwards called in question. The slow evaporation of diabetic urine saturated with common salt furnishes well-formed crystals, but without sufficient lustre to admit of measurement. They contain on an average 23.01 per cent. chloride of sodium, and lose 3.35 per cent. water at  $130^\circ \text{C.}$  (Städeler.)

Instead of the crystals *b*, crystals are sometimes obtained containing between 1 and 2 at. glucose to 1 at. chloride of sodium: probably because the compounds *b* and *c* crystallise together. (Städeler.)

*c.* *With more than 1 at. chloride of sodium.*—By evaporating diabetic urine saturated with common salt, very small crystals are sometimes obtained, which contain  $1\frac{1}{2}$  per cent. water, and more chloride of sodium than the crystals of *b*, corresponding nearly to the formula  $\text{C}^6\text{H}^{12}\text{O}^6\cdot 2\text{NaCl}$ . (Städeler, Pharm. Centr. 1854, 930.)

**Lævoglucose.** This sugar, isomeric with dextroglucose, but distinguished from it by turning the plane of polarisation the opposite way, occurs, together with dextroglucose, in honey, in many fruits, and in other sacchariferous vegetable organs; the mixture of these two sugars in equal numbers of atoms constitutes fruit sugar, or inverted sugar, which is itself lævo-rotatory, because the specific rotatory power of lævoglutucose is greater than that of dextroglucose. This lævo-rotatory inverted sugar was recognised as a substance distinct from cane-sugar, even in the last century, by Lowitz and others, but no certain mode of discrimination was known, till Biot showed that the different kinds of sugar may be distinguished from one another by their optical rotatory power.

Lævoglucose was first obtained as a distinct substance by Dubrunfaut (Ann. Ch. Phys. [3] xxi. 169). Its isolated occurrence has not been demonstrated with certainty; nevertheless some kinds of apple and pear contain more lævo- than dextro-glucose, perhaps because the mixture of these two substances in equal numbers of atoms, first produced by the inversion of cane-sugar, has already suffered an alteration chiefly affecting the dextroglucose. (Buignet, Ann. Chym. Phys. [3] lxi. 264.)

*Formation.*—1. A solution of cane-sugar left to itself, or warmed with dilute acids, loses its dextro-rotatory power, and acquires a lævo-rotatory power, which, when the transformation, or *inversion*, is complete, amounts to  $38^\circ$  for every  $100^\circ$  of the original rotation to the right. This alteration depends on the assimilation by the cane-sugar of  $\delta$  per cent. (1 at.) water, whereby it is resolved into dextro- and lævoglutucose:



The same decomposition is brought about by contact with yeast, or with the peculiar ferment of fruits (pectase).



2. Lævoglucose is also produced by boiling lævulosan ( $C^6H^{12}O^6$ ) with water or with dilute acids. (Gélis, Compt. rend. xlviii. 1662.)

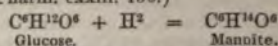
3. Inulin, the amylaceous matter obtained from the roots of *Inula Hellenica*, and many other plants of the composite order, which also has the composition  $C^6H^{12}O^6$ , yields, when boiled with dilute acids, or for a long time with water, a lævo-rotatory sugar, which, according to Dubrunfaut, is identical with the lævoglucose obtained by method 1.

*Preparation of Lævoglucose from inverted sugar.*—When 10 grms. of inverted sugar prepared from cane-sugar by the action of acids as above mentioned, are intimately mixed with 6 grms. hydrate of lime and 100 grms. water, the mass, which is liquid at first, solidifies after a certain amount of agitation, and yields, by strong pressure, a solution of the calcium-compound of dextro-glucose; while the solid residue, washed and decomposed with oxalic acid, yields lævoglucose (Dubrunfaut). The inverted sugar occurring in fruits may be decomposed in the same manner.

*Properties.*—Lævoglucose is a colourless uncrystallisable syrup (Dubrunfaut), an amorphous solid mass (Bouchardet). After being heated to  $100^\circ C.$ , it exhibits the composition  $C^6H^{12}O^6$ . It is as sweet as cane-sugar, and acts as a purgative. It is more soluble in alcohol than dextro-glucose. Its rotatory power varies with the temperature. For the transition-tint,  $[\alpha] = -106^\circ$  at  $14^\circ C.$ ;  $= -79.5^\circ$  at  $51^\circ C.$ ;  $= -53^\circ$  at  $90^\circ C.$  (Dubrunfaut.)

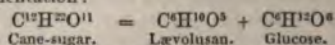
*Decompositions.*—Lævoglucose, when heated, yields a product analogous to the glucosan (p. 864) of dextro-glucose, but more easily decomposable (Gélis, Compt. rend. li. 331); probably, therefore, lævulosan.—Lævoglucose in contact with yeast undergoes vinous fermentation without previous conversion into another kind of sugar (Dubrunfaut).—The other reactions of lævoglucose have been studied only with fruit-sugar containing dextro-glucose: they agree with those of dextro-glucose.

When sodium-amalgam is added to an aqueous solution of cane-sugar inverted by the action of dilute sulphuric acid, the excess of acid having been removed, evolution of hydrogen ceases altogether as soon as the liquid has become slightly alkaline; heat is evolved; and, when the action is complete, the solution is found to contain mannite (Linnemann, Ann. Ch. Pharm. cxxiii. 136.)



*Combination.*—With Lime.—Lævoglucose forms with lime a soluble basic compound analogous to that of dextro-glucose (p. 862), which absorbs oxygen from the air and decomposes.—A second compound containing 3 at. lime to 1 at. lævoglucose forms sparingly soluble microscopic needles, and is decomposed by water when exposed to light and air, the compound deliquescent and the sugar undergoing decomposition (Dubrunfaut.)

*Lævulosan.*  $C^6H^{12}O^6$ . (Gélis, Compt. rend. xliii. 1062; Ann. Ch. Phys. [3] lvii. 234; Jahresb. 1859, p. 547.)—Cane-sugar quickly heated to  $160^\circ C.$ , and kept in the melted state at that temperature for a moderate time, is converted into a mixture of equal numbers of atoms of lævulosan and dextro-glucose, the latter of which may be removed by fermentation:



The remaining liquid, which has a lævo-rotatory power  $= 15^\circ$  for the transition tint, leaves, when evaporated, a syrup, which does not crystallise even when kept 5 years, but contains lævulosan, partly unaltered, partly metamorphosed.

Lævulosan is converted by boiling water and by dilute acids into a fermentable lævo-rotatory sugar, which reduces copper-solution, and is probably identical with lævoglucose.

**GLUCOSE, DETECTION AND ESTIMATION OF.** The reactions best adapted for the detection of glucose (dextro- or lævo-) in solution, either alone or in presence of cane-sugar, are:—1. The dark brown coloration with *potash-ley* (18, p. 860) cane-sugar not exhibiting any sensible coloration when thus treated.—2. The black brown coloration and greyish brown precipitate forming by *basic nitrate of bisulphate* in the solution mixed with carbonate of sodium (21, p. 860).—3. The reduction of *cupric salts*. It is necessary to observe, however, that cane-sugar reduces cuprous oxide from an alkaline solution of cupric sulphate after prolonged boiling, being in fact thereby partly converted into glucose; but with glucose the reduction is immediate (25, p. 860).—4. The decoloration of an alkaline solution of *ferricyanide of potassium* (30, p. 861), an effect not produced by cane-sugar.—5. The non-production of a violet-blue precipitate with *nitrate of cobalt* and caustic alkali, indicates the presence of glucose in a solution previously known to contain cane-sugar (24, p. 860).—6. In the solid state or in that of strong syrup, glucose and cane-sugar may be distinguished



by their different behaviour with strong *sulphuric acid* (10, p. 859), glucose simply dissolving, without coloration, whereas cane-sugar is blackened and completely decomposed. This reaction will not, however, serve to indicate the presence of glucose when mixed with cane-sugar.

For the detection of sugar in urine, see URINE.

**Quantitative Estimation.**—1. By reduction of *cupric salts*. A known measure of potassio-tartrate of copper mixed with potash-ley is heated to boiling in a capsule, and the liquid containing sugar is dropped in until the copper-solution has become colourless by the separation of red cuprous oxide. The quantity of glucose required to reduce the quantity of copper-solution employed must be ascertained by a preliminary experiment. Barreswil (J. Pharm. vi. 361) prepares the copper-solution by dissolving 400 grms. carbonate of sodium, 500 grms. cream of tartar, 300 grms. sulphate of copper, and 400 grms. hydrate of potassium, in half a litre of water. Fehling (Ann. Ch. Pharm. lxxii. 106; cvi. 75) adds to a solution of 160 grms. neutral tartrate of potassium (or better, 192 grms. tartrate of potassium and sodium) in a small quantity of water, 600 or 700 c.c. soda-ley of sp. gr. 1.12, then a solution of 40 grms. crystallised sulphate of copper in about 160 c.c. water, and dilutes the mixture until it measures 1154.4 c.c. at 15° C. Five milligrammes of dry glucose can reduce 1 c.c. of this solution. The solution must be kept in well closed vessels, to protect it from carbonic acid and air; it ought not to give any precipitate of cuprous oxide when boiled by itself. The sugar-solution to be tested is best employed free from acid.

2. When a solution contains no optically active substance besides glucose, or only cane-sugar in addition, the quantity of dextroglucose may be deduced from its rotatory power. (See SACCHARIMETRY.)

3. Glucose, as well as cane-sugar, may also be estimated by the quantities of carbonic anhydride and alcohol produced from it by fermentation with yeast. According to Pasteur, 100 pts. cane-sugar, or 105 pts. glucose, yield by fermentation 49.12 pts. carbonic anhydride and 51.01 pts. absolute alcohol. (See SUGAR and SACCHARIMETRY.)

**GLUCOSE FERMENT.** The conversion of cane-sugar into glucose (inversion of sugar) which takes place in vinous fermentation, is regarded by Pasteur as a secondary effect, depending on the action of the succinic acid, which is always produced in small quantity in that process. According to Berthelot, on the other hand (Compt. rend. li. 980; Jahresb. 1860, p. 518), the change is due to the action of a peculiar ferment, contained in or produced from yeast. That it does not depend on the action of a free acid, is shown by the fact that when yeast is added to a solution of cane-sugar made alkaline by addition of acid carbonate of sodium, a considerable quantity of inverted sugar is produced, although the fermentation is retarded by the presence of the alkali. When the liquid obtained by diffusing yeast in a twofold quantity of water, leaving it to stand for several hours in the cold, and filtering, is added to a solution of cane-sugar mixed with a small quantity of acid carbonate of sodium, the inversion of the sugar takes place, though the liquid does not become acid, and no vinous fermentation is set up. On mixing this same liquid with an equal volume of alcohol, white flocks are precipitated, which, when washed with alcohol and dried at ordinary temperatures, form a yellow horny mass, consisting, according to Berthelot, of a nitrogenous substance analogous to diastase and pancreatin, which may be redissolved in water, and afterwards coagulated by heat or by nitric acid. One part of this substance is sufficient to convert from 50 to 100 pts. of cane-sugar into glucose. It appears to be formed from the yeast itself; for if yeast which has been washed for any length of time with water—provided it has not become putrid—be left for some time in contact with water, it still gives up to the water this so-called glucose-ferment. (Berthelot.)

**GLUCOSIDES.** *Glucosamides, Saccharogens.*—These terms were applied by Laurent (Ann. Ch. Phys. [3] xxxvi. 330) to substances which, when decomposed by dilute acids, yield, on the one hand, dextroglucose or another saccharine substance isomeric therewith, and, on the other, a product differing in character according to circumstances, but not belonging to the class of carbohydrates  $C^mH^nO^p$ . These bodies are natural products occurring frequently in the bodies of plants, less frequently in those of animals; none of them have been prepared artificially.

Berthelot's class of *Saccharides* includes, besides these, certain artificially prepared compounds of the carbohydrates with acids. (See SACCHARIDES.)

The resolution of glucosides into glucose, or a corresponding product, and a second body, takes place for the most part on boiling with dilute *mineral acids*; or it is produced by heating the glucoside with aqueous *alkalis* or *baryta-water*. In this latter case, according to Rochleder (Wien. Akad. Ber. xxiv. 32), crystallisable sugar is sometimes obtained, whereas the decomposition with acids yields only uncrystallisable

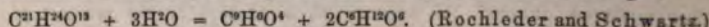
sugar. Or the separation is effected at mean temperature, and in presence of water, by nitrogenous substances occurring either in the same plants as the glucosides, or in others. Emulsin decomposes amygdalin and many other glucosides; myrosin decomposes myronic acid; erythrozym decomposes rubian. Some glucosides are likewise decomposed by yeast and by saliva. The products of the decomposition are often further altered by the action of the air or of the acid employed.

For the separation of the decomposition-products of the glucosides, Rochleder gives the following method. The substance, contained in a flask, is treated with dilute hydrochloric acid, the flask being connected, on the one side with a carbonic acid apparatus, on the other with a Liebig's condensing tube. The air contained in the flask is displaced by carbonic anhydride, and the flask is heated in the water-bath, or, if necessary, in a chloride-of-calcium bath. As soon as the decomposition is complete, the contents of the flask are left to cool in a stream of carbonic anhydride; any product that may have separated out is collected; and the filtrate containing the sugar, hydrochloric acid, and sometimes other soluble products of the decomposition, is mixed with pure carbonate of lead, the addition of which is continued as long as effervescence ensues, after which it is washed, and white lead (prepared by precipitating basic acetate of lead with carbonic acid, and washing) is added, whereby basic chloride of lead is precipitated. The precipitate is collected on a filter and carefully washed; and moist phosphate of silver is added to the filtrate as long as any reaction ensues between this salt and the dissolved chloride of lead, and till the yellow colour of the phosphate of silver remains visible. The liquid is then filtered; any silver that may be dissolved in the filtrate is precipitated with a very small quantity of white lead; the liquid is heated till the white colour of the precipitate passes into cream-colour, then cooled, filtered, treated with sulphuric acid, and filtered again; and the filtrate is evaporated. Colourless sugar then remains, in case such sugar was formed by the decomposition of the glucosides, whilst the second decomposition-product, even if originally soluble in water, is generally rendered insoluble by the white lead.

The distilled liquid obtained by heating a glucoside with hydrochloric acid, contains, together with hydrochloric acid, any volatile product that may have been formed in the decomposition. It is neutralised with baryta or carbonate of barium, heated to decompose acid carbonate of barium, and concentrated by evaporation; the greater part of the chloride of barium is removed by crystallisation, the rest by sulphate of silver; and the filtrate is further examined.

The following enumeration of glucosides and their modes of decomposition is taken from *Gmelin's Handbook*, xv. p. 341.

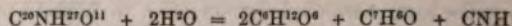
*Asculin* is resolved by heating with dilute acids, into *asculetin* and sugar:



Zwenger and Delffs give other formulæ.

The sugar forms crystals, which melt at  $100^\circ C.$ , are sweeter than grape-sugar, and, like that substance, reduce potassio-cupric tartrate. It is fermentable.

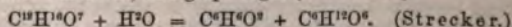
*Amygdalin*, in contact with emulsin and water, is resolved into sugar, bitter almond-oil, and hydrocyanic acid:



(Liebig and Wöhler, 1837). The sugar thus produced is identical in every respect with dextroglucose. (O. Schmidt.)

*Apiin*, boiled with dilute acids, is decomposed, with separation of flocks. The filtrate freed from acid leaves, on evaporation, a sweetish syrup, which, when boiled with potassio-cupric tartrate, separates cuprous oxide, but does not give off the odour of caramel when burnt, does not ferment in contact with yeast, cannot be made to crystallise, and dissolves but partially in alcohol, with separation of yellow flocks. Von Planta and Wallace cannot see in these results any evidence of decomposition, and therefore do not regard *apiin* as a glucoside.

*Arbutin* boiled with dilute acids, or in contact with emulsin, is resolved into hydroquinone (Kawalier's *arcturin*) and grape-sugar (Kawalier):

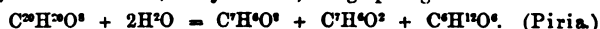


The sugar forms crystals which exhibit the properties of grape-sugar, and when dried at  $100^\circ C.$  or in *vacuo*, contain 36.64 per cent. carbon, 7.05 hydrogen, and 56.31 oxygen, corresponding to the formula  $C^6H^{12}O^6.H^2O$ . (Kawalier, *Wien. Akad. Ber.* ix. 293.)

*Arnica* ( $C^{35}H^{34}O^7$  or  $C^{34}H^{36}O^8$ ) is decomposed by heating with dilute acids, with separation of dark flocks and formation of a substance which reduces cupric oxide. (Walz.)



*Benzohelicin* is resolved, by boiling with dilute acids or aqueous alkalis (not by emulsin), into benzoic acid, salicylic acid, and grape-sugar:



*Bryonin* is resolved by boiling with dilute acids, into bryoretin, hydrobryotin, and sugar:



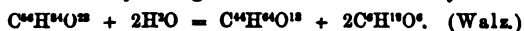
*Caïncin* ( $C^{16}H^{20}O^7$ ) is resolved in like manner, into chiococcaic acid and sugar. (Rochleder and Hlasiwetz.)

*Chitin*, boiled for twelve hours or longer with a mixture of 1 vol. oil of vitriol and 4 vol. water, is resolved, with evolution of ammonia, into amorphous sugar and a second body not yet isolated. Perhaps in this manner:



The sugar is fermentable, and reduces cupric tartrate. (Berthelot, Compt. rend. xlvii. 230.)

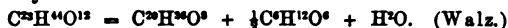
*Colocynthin* is resolved by boiling with dilute acids into colocynthein and sugar:



*Convallarin* is decomposed in like manner into convallaretin and sugar:



*Convallamarin* yields under the same circumstances convallamaretin and sugar:



*Convolvulin* is resolved by sulphuric or alcoholic hydrochloric acid, with assumption of 11 at. water, into convolvulinolic acid and sugar:



*Convolvulin-sugar*. — When Kayser (Ann. Ch. Pharm. li. 98) decomposed convolvulin by passing hydrochloric acid gas into the alcoholic solution, and after leaving the mixture to itself for ten days, extracted the resulting convolvulinol with ether, there remained an acid liquid, which was neutralised with carbonate of lead, filtered and evaporated. From the residue, absolute alcohol extracted a sticky, translucent, sweetish mass, which reduced cupric oxide, yielded crystals when brought into contact with common salt, fermented with yeast, and exhaled the odour of sugar when burnt on platinum-foil. Mayer, after decomposing convolvulinic acid with dilute sulphuric acid, and removing the convolvulinol, saturated the liquid with carbonate of lead; treated the filtrate with sulphuretted hydrogen; evaporated it to  $\frac{1}{10}$ ; removed the separated convolvulin by agitation with ether; evaporated further; and thus obtained a brown sweetish syrup, which behaved like grape-sugar when burnt, also with an alkaline cupric solution, with bile, with sulphuric acid, with water, and with alcohol whether aqueous or absolute, but did not form a crystalline compound with common salt, and could not itself be made to crystallise. This syrup mixed in alcoholic solution with an alcoholic solution of baryta not in excess, formed a precipitate composed like monoglucosate of barium (p. 862). (Mayer, Ann. Ch. Pharm. lxxxiii. 138.)

*Crocin* is resolved by dilute acids into crocetin and crocin-sugar:



*Crocin-sugar*, obtained by decomposing crocin in the manner described above, is easily crystallisable, sweet, and reduces from potassio-cupric tartrate half as much cuprous oxide as dextro-glucose. (Rochleder and L. Mayer, Wien. Akad. Ber. xxix. 6.)

*Cyclamin* solidifies when heated with aqueous hydrochloric acid, with formation of sugar and separation of a second product. (De Luca.)

*Daphnin* is resolved by boiling with dilute acids, into daphnetin and sugar:



*Datiscin*, treated in the same manner, yields datiscetin and sugar:

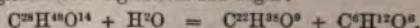


The sugar is obtained by evaporation, after removal of the datiscetin and the sulphuric acid, as a sweet syrup, which solidifies in the semi-crystalline form after standing for some time, and reduces potassio-cupric tartrate at 100° C. (Stenhouse, Ann. Ch. Pharm. xcvi. 171.)

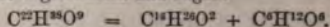


Walz's *Digitalin* is resolved by boiling with dilute sulphuric acid, into digitaliretin, paradigitalletin and sugar. Walz supposes the reaction to consist of two stages:

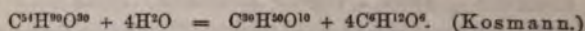
a. Resolution of digitalin into digitaletin and sugar:



b. Further decomposition of the digitaletin, partly, with abstraction of 2 at.  $H^2O$ , into paradigitalletin, partly into digitaliretin and sugar:

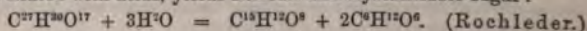


Walz's digitaletin decomposed by dilute acids yields the products above mentioned (Walz, Delffs). Kosmann's *digitalin* and *digitalic acid*, which differ from Walz's compound in composition and properties, are resolved by dilute acids into digitaliretin (which however is not the same as Walz's) and sugar. Decomposition of digitalin:

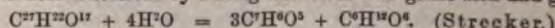


*Euxanthic acid* ( $C^{21}H^{18}O^{11}$ ) is, according to W. Schmidt (Ann. Ch. Pharm. xciii. 88), a glucoside, which is decomposed by sulphuric acid into euxanthone and sugar. According to Erdmann, the products formed in this reaction are euxanthone and hamathionie acid (lead salt =  $C^4H^7O^{12}.SO^2.3PbO$ ); on the other hand, euxanthic acid decomposed by heat yields euxanthone,  $C^{20}H^{12}O^6$ , carbonic anhydride, and water. The latter decomposition, as well as the formulæ of euxanthic acid and euxanthone, is inconsistent with Schmidt's supposition; nevertheless, Erdmann's hamathionie acid bears some resemblance to sulphamidonic acid and other compounds of like nature. (Kraut.)

*Fraxin*, heated with acids, yields fraxetin and crystallisable sugar:



*Gallotannic acid* is resolved by boiling with acids into gallic acid and glucose:



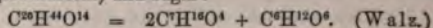
The sugar exhibits the reactions and composition of dextroglucose. (Strecker, Ann. Ch. Pharm. xc. 331.)

By heating 50 grms. gallotannic acid with 50 grms. oil of vitriol and 450 grms. water to  $90^\circ C$ . for three days, and filtering off the gallic acid, a black saccharine solution is obtained which when neutralised with carbonate of lead, mixed with a slight excess of neutral acetate of lead, concentrated, freed from lead by sulphuretted hydrogen, and decolorised by animal charcoal, agrees perfectly with grape-sugar in rotatory power, fermentation, and reaction with potassio-cupric tartrate. (Buignet, Ann. Ch. Phys. [3] lxi. 287.)

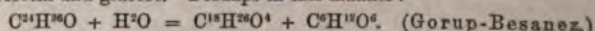
The iodine-compound of a tannin occurring in sweet fruits is likewise decomposed, with formation of dextroglucose, by boiling with dilute sulphuric acid. (Buignet.)

*Gelatin*.—When isinglass is boiled for some days with dilute sulphuric acid, sulphate of ammonia is formed together with a fermentable sugar (Gerhardt, *Traité* iv. 509). Hyalin-cartilage and rib-cartilage, boiled with hydrochloric acid, yield large quantities of glucose. (Fischer and Bodeker, Ann. Ch. Pharm. cxvii. 111.)

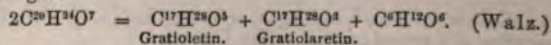
*Globularin*, boiled with dilute sulphuric acid, yields globularetin (part of which changes into paraglobularetin) and sugar:



*Glycyrrhizin* is resolved, when its aqueous solution is boiled with hydrochloric acid, into glycyrretin and glucose. Perhaps in this manner:

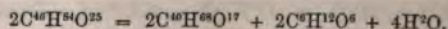


*Gratiolin* is resolved by boiling with dilute sulphuric acid into gratioletin, gratiolaretin, and sugar:

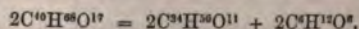


Gratioletin. Gratiolaretin.

*Gratiosolin* in contact with aqueous acids or alkalis is resolved into gratiosoletin and sugar:



The *gratiosoletin* thus formed is further resolved by boiling into hydrogratiosoleretin and sugar:



Part of the hydrogratiosoleretin is further converted, with elimination of 2 at. water, into gratiosoleretin,  $C^{31}H^{52}O^8$ . (Walz.)

*Helianthic acid*.—This name is applied by Ludwig and Kromayer (N. Br. Arch.

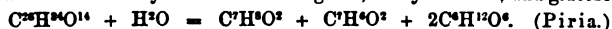
xcix. 1, 285) to a substance obtained from the seed of the sunflower (*Helianthus annuus*), which is insoluble in cold water and in alcohol, not fermentable, and reduces potassio-cupric tartrate only after boiling with acids.

*Helicin* heated with acids or alkalis, or in contact with emulsin or yeast, is resolved into salicylous acid and dextroglucose:



*Chlorhelicin* ( $C^{12}H^{13}ClO^7$ ) exhibits a similar reaction, yielding, however, chlorosalicylous instead of salicylous acid. (Piria.)

*Helicoidin* is resolved by emulsin into saligenin, salicylous acid, and glucose:



*Indican* is resolved by acids or alkalis, *indicanin* by acids, into indiglucin and other products (Schunck). See *INDICAN*.

*Jalappin* in contact with dilute mineral acids is resolved into jalappinol and sugar:



*Jalappic acid*, which contains 3 at. water more, is decomposed in like manner, with assumption of 8 at. water. (W. Mayer.)

The *Lycopodium-bitter* of Kamp and Bödeker reduces potassio-cupric tartrate after boiling with dilute acids, but not in its unaltered state, and should therefore perhaps be regarded as a glucoside.

*Menyanthin*, boiled with dilute sulphuric acid, is resolved into sugar and an oil which smells like bitter almonds. (Ludwig, N. Br. Arch. cviii. 84.)

*Myronate of potassium* is decomposed in contact with myrosyn and water, yielding oil of mustard, sugar, and other products (Ludwig and Lange, Zeitschr. Ch. Pharm. iii. 577). The formula  $C^{22}NH^{16}S^4O^{18}.KO$  ( $= C^4NH^4S^2 + KO.S^2O^4 + C^{12}H^{12}O^{14}$ ) given by Ludwig and Lange, is, according to Will and Körner (Ann. Pharm. cxix. 376), more correctly  $C^{22}NH^{16}KS^4O^{22}$ , and contains the elements of oil of mustard,  $C^4NH^4S^2$ , glucose,  $C^{12}H^{12}O^{12}$ , and acid sulphate of potassium,  $S^2KHO^2$ . Ludwig and Lange also found sulphate of potassium among the products of the reaction, but no sulphite.

*Ononin* is resolved by boiling with dilute acids, into formonetin and glucose (Hlasiwetz):



*Onospin* is resolved under similar circumstances into ononetin and sugar (Hlasiwetz):



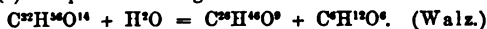
Such is the view of the reaction given by Limpricht (Grundr. d. org. Chem. Braunsch. 1864, 680.) For Hlasiwetz's formulae, see *FORMONETIN* (p. 696) and *ONONIN*.

The sugar formed from ononin and onospin by the action of dilute sulphuric acid, remains in solution after the second product of the decomposition has been removed by filtration, the sulphuric acid by carbonate of lead, and the excess of lead by sulphuretted hydrogen, and is obtained by evaporation as a very sweet fermentable syrup, in which granular crystals form after a few days. These crystals melt at the heat of the water-bath to a viscid syrup which remains soft after a day's drying, and exhibits all the reactions of grape-sugar. (Hlasiwetz, Wien. Akad. Ber. xv. 153.)

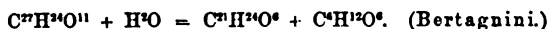
*Paristypnin* boiled with dilute sulphuric acid is resolved into paridin and sugar:



The *paridin* thus produced is resolved by boiling with a larger quantity of dilute sulphuric acid (?) into paridol and sugar:

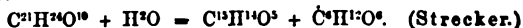


*Phillyrin* is resolved, by boiling with dilute hydrochloric acid, into phillygenin and sugar; by lactic fermentation into phillygenin and the products of the decomposition of sugar:

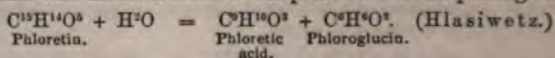


From the solution freed from phillygenin and hydrochloric acid by carbonate of lead, the sugar crystallises, after evaporation and re-solution in alcohol, in warty masses, exhibiting the properties of grape-sugar. (Bertagnini, Ann. Ch. Pharm. xcii. 110.)

*Phlorhizin* is decomposed by dilute acids, not by emulsin, yielding phloretin and sugar (Stas):

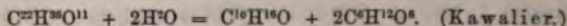


*Phloretin* boiled with alkalis is resolved into phloretic acid and phloroglucin :

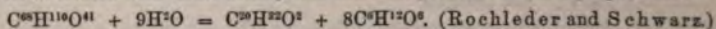


Phlorhizin-sugar is difficult to crystallise, and exhibits the properties and composition of crystallisable grape-sugar (Stas, Ann. Pharm. xxx. 200). It reduces the same quantity of cupric oxide as dextroglucose. (Roser, Ann. Ch. Pharm. lxxiv. 178.)

*Pinipicrin* splits up into ericicol and sugar when its aqueous solution is heated with acids :

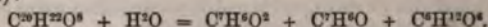


*Ericolin* treated with dilute acids yields the same products in other proportions :

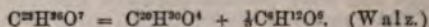


The sugar produced from pinipicrin is rendered uncrystallisable by the foreign substances contained in it; at 100° C. it becomes soft; at common temperature it is solid and brittle, and is easily reduced to a yellowish powder containing 2 per cent. ash, and after deduction of this, 39.06 per cent. C, 6.62 H, and 54.32 O, corresponding approximately to the formula  $\text{C}^6\text{H}^{12}\text{O}^6$ . (Kawalier, Wien. Akad. Ber. xi. 352.)

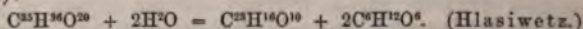
*Populin*, when boiled with dilute acids, splits up into benzoic acid, saliretin and glucose (Piria):



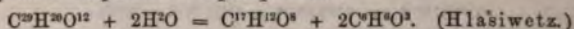
*Prophetin* is decomposed, by boiling with hydrochloric acid, into properetin and sugar:



*Quercitrin* is decomposed by dilute sulphuric acid into quercetin and quercitrin-sugar (Rigaud):

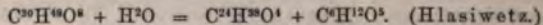


*Quercetin* is further decomposed by boiling with potash-ley into quercetic acid and phloroglucin (Hlasiwetz). The same products are obtained, but in different proportions by the decomposition of *Alpha-quercetin*:



*Quercitrin-sugar* is obtained as a light-yellow syrup, which solidifies in a crystalline mass on standing for a few days over sulphuric acid, by filtering off the quercetin, separating the sulphuric acid by carbonate of barium, evaporating on the water-bath, decolorising with animal charcoal, and again evaporating. It has a sweeter taste than dextroglucose, and does not rotate the plane of polarisation. Dried in vacuo, it contains 34.78 per cent. C, 7.24 H, and 57.98 O, corresponding to the formula  $\text{C}^{25}\text{H}^{36}\text{O}^{12} \cdot 3\text{H}^2\text{O}$  (calc.: 34.65 per cent. C, 7.47 H). When warmed with potassio-cupric tartrate, it immediately reduces the same quantity of cuprous oxide as would be reduced by dextroglucose. (Rigaud, Ann. Ch. Pharm. xc. 195.)

*Quinovin* is resolved by alcoholic hydrochloric acid into quinovic acid and quinovin-sugar:



*Quinovin-sugar* is obtained from the alcohol containing hydrochloric acid after separation of the quinovic acid, either by Rochleder's method (p. 866), or as follows:—The liquid is neutralised with anhydrous carbonate of sodium (or carbonate of lead), and filtered; the precipitate washed with a small quantity of strong alcohol; the alcohol distilled off; and the remaining liquid evaporated to dryness over the water-bath. The thick residue is dissolved in water, the solution filtered from the undissolved portion is evaporated, and the residue is digested in absolute alcohol. The alcoholic solution when evaporated leaves the quinovin-sugar, to be purified, if necessary, by re-solution and decoloration with animal charcoal. It is an amorphous, solid, deliquescent mass, having a faint, somewhat bitter taste; it gives off water when continuously heated over the water-bath. Dried at 100° C., it contains 43.34 per cent. carbon, 7.72 hydrogen, and 48.94 oxygen, answering to the formula  $\text{C}^6\text{H}^{12}\text{O}^6$ . It is isomeric or identical with mannitan; smells like caramel when heated; reduces potassio-cupric tartrate only in concentrated solution; dissolves completely in alcohol. (Hlasiwetz, Ann. Ch. Pharm. cxi. 118.)

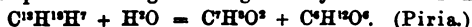
*Quinovatannic acid* is resolved, by boiling with dilute sulphuric acid, into quinovaric acid, and a substance which behaves with cupric sulphate and potash-ley like grape-sugar. (Hlasiwetz.)



Schunck's *Rubianic acid* splits up into alizarin and sugar when boiled with dilute sulphuric acid, or with aqueous alkalis, or by contact with water and erythrozym.  $C^{32}H^8O^{21} + 5H^2O = 2C^{14}H^2O^4 + 2C^{12}H^{12}O^{11}$ .—Rochleder's *Ruberythric acid*,  $C^{72}H^{36}O^{46}$  or  $C^{36}H^{18}O^{23}$ , perhaps identical with the last substance, yields the same products when heated with hydrochloric acid,  $C^{72}H^{36}O^{46} = 3C^{16}H^2O^4 + C^{12}H^{12}O^{11} + 10H^2O$ , or  $C^{36}H^{18}O^{23} = 2C^{16}H^2O^4 + 1\frac{1}{2}C^{12}H^{12}O^{11} + 3H^2O$ . (Rochleder.)

In the complicated decomposition of Schunck's *Rubian* by the same reagents and by chlorine, sugar is obtained together with various other bodies. *Rubihydran* and *Rubiedehydran* behave in the same way. (Schunck.)

*Salicin* is decomposed into saligenin and glucose by contact with emulsin:



The sugar is in every respect identical with dextroglucose (Schmidt). By boiling with dilute acids, saliretin is obtained in place of saligenin. (Piria.)

*Saponin* is decomposed into sapogenin and saponin-sugar, or glucose when boiled with dilute acids (Overbeck, Rochleder and Schwarz). *Scenegin* (isomeric with saponin, according to Bolley) yields, besides sapogenin, a substance which reduces potassio-cupric tartrate. (Bolley.)

*Saponin-sugar* remains in solution after the sapogenin has been filtered off, the acid removed by carbonate or oxide of lead, and the excess of lead by sulphydric acid and by treatment with animal charcoal and evaporation is obtained as a tasteless, yellowish brown residue, easily soluble in water (Rochleder and Schwarz, Wien. Akad. Ber. xi. 339). When saponin is decomposed with dilute sulphuric acid, glucose remains in solution, after removal of the excess of acid, and may be obtained crystallised by evaporation. It has a sweet taste, and reduces an alkaline solution of cupric oxide in the cold (Overbeck, N. Br. Arch. lxxvii. 135). Crawford obtained gum, but no sugar from saponin, by means of dilute sulphuric acid (Pharm. Viertelj. vi. 361). Saponin-sugar dried at 100° C. contains, according to Rochleder and Schwarz, 41.99 per cent. C, 6.55 H, and 51.46 O, corresponding to the formula  $C^{22}H^{20}O^{11}$ .

*Scammony resin* ( $C^{34}H^{40}O^{16}$ ) and *Scammonic acid* ( $C^{34}H^{40}O^{16} \cdot \frac{1}{2}H^2O$ ) split up into scammonolic acid and sugar when boiled with dilute acids (or with baryta-water):

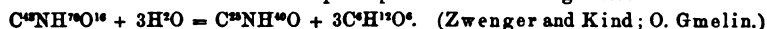


Like jalappin (p. 869), therefore, but with this difference, that instead of the product corresponding to jalappinol (which is converted by strong bases into jalappic acid) a product containing 1 at. water less is formed. (Spirgatis.)

The sugar remains in solution after separation of the scammonolic and sulphuric acids, and can be obtained in sweet-tasting laminæ grouped in cauliflower-like shapes, which behave like glucose with sulphate of copper and potash-ley, when heated and when fermented. (Spirgatis, Ann. Ch. Pharm. cxvi. 305.)

*Smilacin* is slowly decomposed when boiled with hydrochloric acid, with separation of a jelly and formation of sugar. (O. Gmelin, Delffs, Walz.)

*Solanin* boiled with dilute acids splits up into solanidin and glucose:

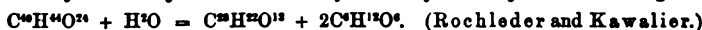


The sugar crystallises well, and possesses the reactions and compositions of dextroglucose (Zwenger and Kind, Ann. Ch. Pharm. cxviii. 149). Rotatory power not determined.

*Thujin* is decomposed by heating its alcoholic solution with dilute acids, into thujetin and sugar:

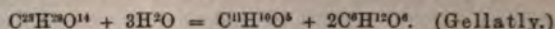


When it is heated for a shorter time, thujinenin,  $C^{14}H^{14}O^7$ , may also be formed in place of the thujetin. Thujin heated with baryta-water yields thujetic acid and sugar:



When thujin has been decomposed by acids, the sugar remains in solution after removal of the thujetin and sulphuric acid (by carbonate of barium), and, by evaporation and drying at 100° C., is obtained as a colourless mass, which is easily reduced to a white powder when cold, and contains 39.83 per cent. C, and 6.81 H, corresponding to the formula  $C^8H^{12}O^6$ ; its aqueous solution does not crystallise even after standing for several months; it reduces the same quantity of cupric oxide as dextroglucose. The sweet sugar of the same composition produced by the action of baryta-water solidifies (after the removal of the baryta by dilute sulphuric acid, of the excess of sulphuric acid by basic acetate of lead, and of the lead by sulphydric acid) to a crystalline mass when its solution is allowed to stand a short time after evaporation on the water-bath. (Rochleder and Kavalier, Wien. Akad. Ber. xxix. 12.)

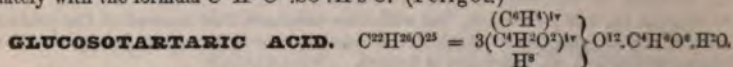
*Xanthorhamnin* is decomposed by boiling with dilute acids into rhamnetin and sugar:



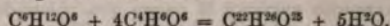
**GLUCOSOCITRIC ACID.**  $C^{22}H^{30}O^{14} = \frac{(C^6H^{12}O^6)^4}{2(C^4H^4O^5)^2} \left\{ O^{12}.4C^6H^{12}O^6.5H^2O = C^6H^{12}O^6 + 8C^4H^4O^5 - 2H^2O. (?) \right\}$ —The calcium-salt of this acid, prepared in a similar manner to that of glucosotartaric acid (see below) appears to contain  $C^{22}H^{30}O^{14}.Ca^{10}O^{10}.2H^2O$ . (Berthelot, Ann. Ch. Phys. [3] liv. 81.)

**GLUCOSOSUCCINIC ACID.** A mixture of cane-sugar and succinic acid in equivalent proportions heated to between  $120^\circ$  and  $130^\circ$  C. melts to a brown syrup, with elimination of water. The product is an acid compound of glucose with succinic acid, which decomposes at  $100^\circ$  C. with formation of humus, and forms with lime a salt soluble in water, insoluble in alcohol. (Van Bemmelen, Jahresb. d. Chem. 1858, p. 436.)

**GLUCOSOSULPHURIC ACID.** *Sulphosaccharic acid.*  $C^{24}H^{40}O^{22}.SO^4. (?)$  (Peligot, Ann. Ch. Phys. [2] lxvii. 168.)—To prepare this acid  $1\frac{1}{2}$  pt. strong sulphuric acid is added, by small portions, to 1 pt. of glucose melted at the heat of the water-bath, the mixture being continually stirred, and the vessel, if necessary, plunged into cold water. If the glucose is impure, or the heat rises too high, the product becomes somewhat brown, which, however, does not affect the purity of the lead-salt. The mixture, diffused in a large quantity of water, is saturated with carbonate of calcium; acetate of barium is added to the filtrate as long as a precipitate of sulphate of barium is thereby produced; and the liquid, again filtered, is precipitated with basic acetate of lead. If the liquid, after precipitation with acetate of barium, still remains brown, the colouring matter is removed by a small quantity of basic acetate of lead, and the pure salt is precipitated from the filtrate by a larger quantity. The precipitate, washed, and decomposed under water with sulphydric acid, yields *aqueous glucososulphuric acid*, which tastes at the same time sour and sweet, reddens litmus, decomposes when evaporated in vacuo, and more quickly over the water-bath, into glucose and sulphuric acid, and forms salts, almost all of which are soluble. The *lead-salt* gives by analysis 18.16 per cent. carbon, 2.4 hydrogen, 4.50  $SO^4$ , and 53.2 to 55.3  $Pb^2O$ , agreeing approximately with the formula  $C^{20}H^{30}O^{20}.SO^4.4Pb^2O$ . (Peligot.)



*Glucotetratartaric acid* (Berthelot, Ann. Ch. Phys. [3] liv. 78).—This acid is produced by heating dextroglucose with tartaric acid:



It appears to exist in grapes at the time of ripening. When expressed grape-juice is saturated with chalk, filtered, strongly concentrated, filtered again, precipitated with 2 vol. alcohol, and the precipitate purified by washing with weak alcohol, re-solution in water, and re-precipitation with alcohol, a calcium-salt is obtained which reduces potassio-cupric tartrate like glucosotartrate of calcium, and is resolved by acids into dextroglucose and an acid which exhibits the characters of tartaric acid.

*Preparation of the calcium-salt.*—An intimate mixture of equal parts of dextroglucose and tartaric acid is heated for a day or two to  $120^\circ$  C. in an open vessel; the cooled mass is triturated with carbonate of calcium and a small quantity of water, and the liquid is filtered. Tartrate of calcium, with the excess of carbonate, then remains on the filter, while the solution contains the salt of the new acid, together with excess of glucose. On precipitating this solution with twice its volume of alcohol, collecting the precipitate, washing it with dilute alcohol, dissolving in water, again precipitating with alcohol, and repeating the same series of operations a third time, the calcium-salt is obtained free from sugar. It is dried for a week or fortnight in vacuo, then completely by heating it to  $110^\circ$  C.

*Aqueous glucosotartaric acid* is obtained by decomposing the calcium-salt with excess of oxalic acid.

The aqueous solution of the acid and of its salts is gradually resolved by boiling into dextroglucose and tartaric acid, the decomposition being accelerated by a small quantity of sulphuric acid. The calcium and magnesium-salts reduce potassio-cupric tartrate. The acid is not fermentable.

Glucosotartaric acid is tetrabasic. The salts still retain water at  $110^\circ$  C. The *calcium-salt*,  $C^{22}H^{30}O^{23}.Ca^{10}O^{10} + 2 \text{ aq.}$ , is a white amorphous powder, which gives off 14.1 per cent. water at  $110^\circ$ . The *magnesium-salt*,  $C^{22}H^{30}O^{23}.2Mg^{10}O^{10} + 5 \text{ aq.}$ , gives off, after drying in vacuo, 26.4 per cent. water at  $110^\circ$ . There are two *lead-salts*,



$C^{22}H^{22}Pb^{10}O^{23}$ , which is insoluble, or becomes so during preparation, and  $C^{22}H^{22}Pb^{10}O^{23}$ , which is soluble, and after drying in vacuo, gives off 10.9 per cent. water at  $110^{\circ}$ .

**GLUE.** An inspissated jelly made from the parings of hides and other offal, by boiling them in water, straining through a wicker basket, suffering the impurities to subside, and then boiling it a second time. The articles should first be digested in lime-water, to cleanse them from grease and dirt; then steeped in water, stirring them well from time to time; and lastly, laid in a heap to press out the water, before they are put into the boiler. Some manufacturers recommend that the water should be kept as near as possible to a boiling heat, without suffering it to enter into ebullition. The glue is poured into flat frames or moulds, cut into square pieces when congealed, and afterwards dried in a coarse net. It is said to improve by age; and that glue is reckoned the best which swells considerably without dissolving, by three or four days' infusion in cold water, and recovers its former dimensions and properties by drying.

Shreds or parings of vellum, parchment, or white leather, make a clear and almost colourless glue. (For the details of the manufacture, see *Ure's Dictionary of Arts, &c.*, ii. 376.)

**GLUTEN.** Wheat-flour made into a paste, and washed with a large quantity of water, separates into three distinct substances:—vegetable albumin, which is dissolved by the water, together with a little sugar and dextrin, and may be separated from it by evaporation; starch, which is suspended in the fluid, and subsides to the bottom by repose; and gluten, which remains in the hand, and is tenacious, very ductile, somewhat elastic, and of a light brown-grey colour.

The gluten, though it existed before the washing in the pulverulent form, and has acquired its tenacity and adhesive qualities from the water it has imbibed, is nevertheless totally insoluble in this liquid. It has scarcely any taste. When dry, it is semitransparent, and resembles glue in its colour and appearance. If it be drawn out thin, when first obtained, it may be dried by exposure to the air; but if exposed to warmth and moisture while wet, it putrefies like an animal substance. Dried gluten applied to the flame of a candle, crackles, swells, and burns, exactly like a feather or piece of horn. Gluten affords the same products by destructive distillation as animal matters. It is easily dissolved by caustic potash, and precipitated from the solution by acids in tumid flocks. Strong acetic acid likewise dissolves it, and leaves it on evaporation in the form of a tenacious mass. When digested in water containing  $\frac{1}{1000}$  or  $\frac{2}{1000}$  of hydrochloric acid, it diffuses itself through the liquid, gradually dissolves, and on filtering, yields a clear liquid which turns the plane of polarisation of a luminous ray to the left, and behaves with heat and with reagents exactly like a solution of albumin. (Bouchardat, *Compt. rend.* xiv. 962.)

In contact with water, gluten undergoes gradual decomposition, swelling up, and giving off considerable quantities of carbonic anhydride, hydrogen, and sulphuric acid. At the same time, it softens and liquefies, while the water which covers it acquires an acid reaction, and takes up leucine, together with phosphate and acetate of ammonia, the gluten all the while acquiring a darker and darker colour, and ultimately dissolving almost entirely. During these several stages of its transformation, gluten possesses the power of acting as a ferment. Thus, if a small quantity of gluten or wheat-flour be added to starch-paste diffused in water, and the mixture be exposed for several hours to a temperature of  $60^{\circ}$  or  $70^{\circ}$  C., it liquefies, becomes transparent and mobile, and ultimately acquires a sweet taste, the starch being converted first into dextrin, and then into glucose.

Gluten exhibits the same percentage composition as the albuminoids; it is not, however, a simple proximate principle, but, as first shown by Taddei (*Giornale fisica di Brugnattelli*, xii. 360), may be separated into two distinct substances, one soluble and the other insoluble in alcohol; and, according to Ritthausen (*J. pr. Chem.* lxxiv. 193, 384), the portion soluble in alcohol may be further resolved into two substances, one called mucin or vegetable casein, the other gluten, gliadin or vegetable gelatin; the portion insoluble in alcohol is called vegetable fibrin.

To separate these substances, Ritthausen proceeds as follows:—Freshly prepared gluten, divided into small fragments, is digested for several hours with alcohol of 80 or 85 per cent. The alcohol is then heated to boiling, and after half an hour the supernatant liquid is filtered, or simply decanted, and the mass of gluten is again heated several times with boiling alcohol of 75 per cent. The united alcoholic liquids become turbid on cooling, and after half the alcohol has been distilled off, they deposit on cooling considerable quantities of flocculent mucin, mixed with gluten and fat, and easily united by agitation.

To purify the mucin thus obtained, it must then be dissolved in alcohol of 50 per cent. and the hot solution filtered through calico, then left to cool, and frequently agitated while the deposit is forming. The clear liquid then retains all the gluten, together with a very small quantity of mucin. The precipitated mucin is transparent, flocculent, and



	Jones.	Mulder.	Boussingault.	Hithausen,
Carbon .	54·6	54·93    54·75	Dried at 100° C.    Dried in vacuo. 53·3    52·8    54·1    53·4	52·49
Hydrogen .	7·4	7·11    6·99	7·5    7·6    7·6    7·7	6·97
Nitrogen .	16·0	18·71    15·71	14·6    14·4    13·5    13·5	18·02
Sulphur .	. .	0·57    0·62	. .    . .    . .    . .	0·85
Oxygen .	. .	. .    . .	. .    . .    . .    . .	21·41
Ash .	. .	. .    . .	. .    . .    . .    . .	0·26

Mucin yielded 0.98 and vegetable fibrin 0.95 per cent. of sulphur. Vegetable fibrin dehydrated by alcohol, forms a pulverulent mass. (Ritthausen.)

The fats of gluten form a yellow oily mass, neutral, having a sweet taste, and mixed with crystals. (Ritthausen.)

Günsberg (J. pr. Chem. lxxxv. 213) has obtained results differing considerably from those of Ritthausen. According to his experiments, the substance described by Ritthausen as mucin or vegetable casein is not a distinct proximate principle, the deposit which separates from alcohol after boiling with gluten, consisting merely of small fragments of suspended fibrin. Moreover, gluten or gliadin, which remains dissolved in the alcohol after separation of this deposit, is itself not a simple proximate principle: for cold water extracts from it a brown substance containing nitrogen and sulphur; and the residue treated with boiling water yields a limpid solution, which on cooling deposits a substance free from sulphur, and containing, when dried at 130° C., 52.77 per cent. carbon, 6.79 hydrogen, 17.66 nitrogen, and 22.78 oxygen. This substance, which has nearly the same composition as animal gelatin, is regarded by Günsberg as the true gluten or vegetable gelatin. The sulphuretted and non-sulphuretted compounds just mentioned may be extracted directly from gluten by successive treatment with cold and hot water without previous solution in alcohol.

The proportions of gluten in wheat-flour vary considerably, according to the conditions of growth, such as climate, soil, manure, temperature, &c. The best wheat-flour contains from 10 to 11 per cent. of dry gluten; inferior kinds from 8 to 9 per cent. In the moist state, gluten weighs about three times as much as when dry.

The flours of barley, rye, and oats differ considerably in proximate constitution from wheat-flour, boiling alcohol extracting from them fatty and resinous matters, but only traces of gluten. Indeed these grains cannot properly be said to contain gluten, but only vegetable fibrin. Neither is gluten found in appreciable quantity in the flour of peas, beans, or lentils. It appears to exist, however, in the juice of the grape, and of many other fruits, being probably held in solution by tartaric or other vegetable acids.

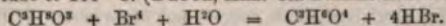
**GLYCERAMINE** or *Glyceryl-hydoramine*.  $C^3H^3NO^2 = \begin{matrix} (C^3H^3)^{'''}/N \\ H^3 \end{matrix} \{ O^2 \} \cdot An$  organic base produced, as a hydrobromate, by passing ammonia-gas into a solution of dibromhydrin in absolute alcohol:



By treating the hydrobromate with strong potash-ley, the base is obtained as an oily liquid easily soluble in water and in ether. *Hydrochlorate of glyceramine* becomes moist on exposure to the air, and decomposes when heated. Its alcoholic solution forms with dichloride of platinum, a double salt,  $C^3H^3NO^2.HClPtCl^2$ , which separates in orange-coloured granules. (Berthelot and De Luca, Ann. Ch. Pharm. ci. 74.)

*Diglyceryl-dihydorbromamine* or *Hemibromhydramide*,  $C^6H^{12}BrNO^2 = \begin{matrix} H^2 \\ (C^3H^3)^{'''}/N \\ (C^3H^3)^{'''}/Br \end{matrix} \{ O^2 \}$ , is an amorphous base, produced by the action of dry ammonia-gas on pure dibromhydrin (Berthelot and De Luca, i. 668); and the analogous compound,  $C^6H^{12}ClNO^2$ , is obtained by heating epichlorhydrin with alcoholic ammonia. (Reboul, p. 898.)

**GLYCERIC ACID**.  $C^3H^3O^4 = \begin{matrix} (C^3H^3O)^{'''}/ \\ H^3 \end{matrix} \{ O^2 \}$ . (Debus, Phil. Mag. [4] xv. 195; Ann. Ch. Pharm. cix. 227; Socoloff, Ann. Ch. Pharm. cvi. 95.)—Produced by the action of nitric acid on glycerin (Debus, Socoloff); by the spontaneous decomposition of nitroglycerin (De la Rue and Müller, Ann. Ch. Pharm. cix. 122); and by heating 1 at. glycerin with 4 at. bromine and a volume of water twenty times as great in a sealed tube to 100° C. (Barth, Ann. Ch. Pharm. cxxiv. 341):



*Preparation*.—1 pt. of glycerin is mixed in a glass cylinder with an equal bulk of water, and 1 pt. of nitric acid of specific gravity 1.5 introduced below it by means of a long-necked funnel (100 grms. glycerin, 100 grms. water, and 100 to 150 grms. red nitric acid are good proportions). The two layers of liquid gradually mix and assume a blue colour, and the oxidation of the glycerin proceeds, accompanied by a copious evolution of gas. If the liquid becomes too hot, the action must be moderated by external cooling. When the oxidation is completed, which takes five or six days, the strongly acid liquid is divided into small portions and evaporated at 100° C. to a syrupy consistence: the united residues are diluted with water, and neutralised with chalk; and the resulting calcium-salts are precipitated by strong alcohol. The liquid (which still contains one or two substances) is carefully separated from the precipitate; the latter is treated with warm water; and the solution filtered from the oxalate of calcium is mixed with a quantity of milk of lime sufficient to produce alkaline reaction, where-



upon the calcium-salt of a peculiar acid is deposited. The liquid separated from this precipitate, freed from excess of lime by carbonic acid, and evaporated to the crystallising point, yields glycerate of calcium, which may be purified by recrystallisation. (Debus). According to Socoloff, when glycerin is mixed with a large excess of nitric acid of specific gravity 1.360, at ordinary temperatures, oxidation begins in a few hours; a large quantity of gas is evolved; crystals of oxalic acid separate in a few days; and the remaining liquid thus formed contains glyceric acid, the calcium-salt of which may be obtained as above.\*

The acid is obtained by decomposing the calcium-salt with a quantity of oxalic acid exactly sufficient to precipitate the lime, and evaporating the filtrate on the water-bath (Debus). Beilstein (Ann. Ch. Pharm. cxx. 226), evaporates the product of the reaction of nitric acid upon glycerin in a large flat-bottomed basin, over the water-bath, dissolves the residue in a large quantity of water, and saturates it with oxide or carbonate of lead. The liquid boiled, filtered, and concentrated by evaporation, deposits, on cooling, crystals of glycerate of lead, which, when purified by recrystallisation, and decomposed by sulphydric acid, yield nearly colourless glyceric acid, as a thick, non-crystallising syrup. The acid, after being heated for some time to  $105^{\circ}\text{C}$ ., is converted into a soft, very tenacious, slightly brown mass, having the composition of *glyceric anhydride*,  $\text{C}^3\text{H}^3\text{O}^3$ , which, at  $140^{\circ}$ , changes to a brownish mass resembling gum arabic; it absorbs water with avidity, and, at a higher temperature, gives off acid vapours, turns brown, and burns with flame. (Debus.)

Glyceric acid is isomeric with pyruvic acid: it is also homologous with glyoxylic acid ( $\text{C}^2\text{H}^2\text{O}^3$ ), and bears the same relation to glycerine,  $\text{C}^3\text{H}^8\text{O}^3$ , that acetic acid bears to alcohol.

Glyceric acid treated with *iodide of phosphorus* yields iodopropionic acid,  $\text{C}^3\text{H}^5\text{IO}^2$  (see PROPIONIC ACID, DERIVATIVES OF). A mixture of glyceric and benzoic acids heated for a long time to  $200^{\circ}\text{C}$ ., appears to yield a benzoglyceric acid. (Beilstein, Ann. Ch. Pharm. cxx. 226.)

The aqueous solution of glyceric acid has an agreeably sour taste, dissolves iron and zinc without evolution of gas, probably forming a lactate or propionate, decomposes carbonates, and coagulates milk. Potash added to a solution of iron in glyceric acid precipitates only a part of the iron; the precipitation of copper from the sulphate by potash is likewise prevented by the presence of glyceric acid, the liquid yielding, however, a dark yellow-brown precipitate when boiled.

*Glycerates*.—Glyceric acid, though a triatomic acid, nevertheless appears to contain only 1 atom of hydrogen replaceable by metals. It is probable, however, that the remaining two atoms of typic hydrogen will be found to be more easily replaceable by acid radicles, just like the second atom of typic hydrogen in glycollic acid (*q. v.*)

The glycerates are soluble in water and crystallise well. They are not reddened by ferrous sulphate, and are thereby distinguished from the pyruvates.

*Glycerate of Ammonium*,  $\text{C}^3\text{H}^3(\text{NH}^4)\text{O}^4$ , forms colourless radiating crystals, which are very deliquescent, melt at a gentle heat, and at higher temperatures turn brown and give off ammonia.

*Glycerate of Barium*,  $\text{C}^3\text{H}^3\text{BaO}^4$ , separates from a hot solution of carbonate of barium in the aqueous acid in large spherical aggregations of concentrically-grouped laminae.

*Glycerate of Calcium*,  $\text{C}^3\text{H}^3\text{CaO}^4 + \text{H}^2\text{O}$ , crystallises in small, white, concentrically-grouped crystals, frequently also in nodules composed of microscopic tables or prisms. By mixing a moderately strong aqueous solution with about an equal volume of hot alcohol, distinct crystals are obtained belonging to the monoclinic system:  $\infty\text{P} \cdot \infty\text{P} \cdot [\infty\text{P}\infty] \cdot \infty\text{P}\infty$ . They have a micaceous lustre, give off their water at about  $120^{\circ}\text{C}$ ., and begin to decompose at  $160^{\circ}$ . The salt is insoluble in alcohol. The aqueous solution precipitates lead, copper, and ferric salts. With nitrate of silver at the boiling heat it forms a black precipitate, and, on addition of ammonia, a specular deposit of silver.

*Glycerate of Lead*,  $\text{C}^3\text{H}^3\text{PbO}^4$ , forms white, hard, anhydrous crystalline crusts.

*Glycerate of Potassium* (acid),  $\text{C}^3\text{H}^3\text{KO}^4 \cdot \text{C}^3\text{H}^3\text{O}^4$ , is obtained in small white crystals by exactly neutralising the acid with carbonate of potassium, adding an equal quantity of the acid, and evaporating to a syrup.

When 1 pt. of *neutral glycerate of potassium* is mixed with 1 pt. of hydrate of potassium dissolved in 2 pts. of water, and the mixture is boiled down till it gives a white precipitate with acetate of lead, after acidulation with acetic acid, the glyceric

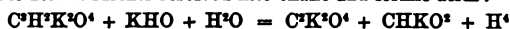
\* When the mother-liquor separated from the crystals of this calcium-salt was mixed with carbonate of potassium in quantity sufficient to precipitate the whole of the lime, and the alkaline filtrate neutralised with nitric acid and concentrated, the syrupy liquid decanted from the crystals of nitre which separated out, yielded needle-shaped crystals with a concentrated solution of acid sulphate of sodium; hence it probably contained a substance of the nature of an aldehyde. (Socoloff.)



acid is found to be resolved into oxalic and lactic acids, the former being precipitated by the acetate of lead, the latter remaining in solution. The glyceric acid is probably first resolved into lactic and malonic acids:



and the malonic acid is further resolved into oxalic and formic acids:



(Debus, Ann. Ch. Pharm. cix. 122). From an experiment made by Atkinson, it appears that glycerate of potassium, when fused with hydrate of potassium, is resolved into acetate and formate of potassium:



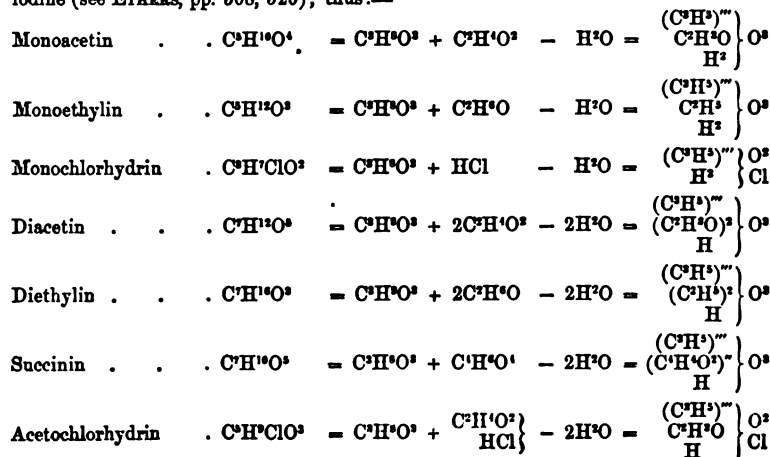
*Glycerate of Silver* is a very unstable salt.

*Glycerate of Zinc*,  $2\text{C}^3\text{H}^5\text{ZnO}^4 + \text{H}^2\text{O}$ , crystallises from a solution of carbonate of zinc in the warm aqueous acid in small colourless crystals, which give off their water at  $140^\circ$ .

**GLYCERIDES.** *Glycerin-ethers. Glyceryl-ethers. Saponifiable Fats.* (Chevreul, *Recherches sur les corps gras d'origine animale*. Paris, 1823.—Berthelot, *Chimie organique fondée sur la synthèse*, ii. 12—164.—Kekulé, *Lehrb. d. org. Chem.* ii. 108—135.)—These bodies are the compound ethers of the triatomic alcohol, glycerin. Some of them exist ready formed, as natural fats, in the bodies of plants and animals, and many more may be produced artificially, by the action of acids upon glycerin.

The names of the glycerides are formed, for the most part, from those of the corresponding acids, by changing the termination *ic* into *in*; thus, acetic acid forms acetins, chlorhydric acid forms chlorhydrins, &c. There are a few glycerides containing monatomic alcohol-radicles instead of acid radicles, and these are designated in like manner; thus, glycerides containing ethyl are called ethylins. The names of glycerides which possess decided acid properties are formed by prefixing the word *glycero* to the name of the acid from which they are formed, *e.g.* glycerotartaric, glycerophosphoric acid, &c.

The formation of glycerides takes place in the same way as that of all other compound ethers, and indeed of all salts whatever, viz. by the union of the acid and base, with elimination of the elements of water (see ACIDS, i. 43, and ETHERS, ii. 509), the number of atoms of water thus eliminated being in the majority of cases equal to the number of atoms of a monobasic acid (or alcohol) concerned in the reaction, or to twice the number of atoms of a dibasic acid, or to three times that of the number of atoms of a tribasic acid. In this manner there are formed three series of normal glycerides, having the constitution of triatomic ethers derived from glycerin,  $\left\{ \begin{smallmatrix} \text{C}^3\text{H}^5 \\ \text{H}^3 \end{smallmatrix} \right\} \text{O}^3$  or  $\left\{ \begin{smallmatrix} \text{C}^3\text{H}^5 \\ \text{H}^3 \end{smallmatrix} \right\} (\text{HO})^3$ , by the replacement of 1, 2, or 3 at. hydrogen by an equivalent quantity of an acid- or alcohol-radicle, or of 1, 2, or 3 at. HO by an equivalent quantity of the peroxide of an acid- or alcohol-radicle or of chlorine, bromine, or iodine (see ETHERS, pp. 508, 520); thus:—



Dichlorhydrin . . .	$C^2H^4Cl^2O$	$= C^2H^2O^3 + 2HCl$	$- 2H^2O = \left( \begin{smallmatrix} C^2H^2 \\ H \end{smallmatrix} \right)^{''} \left\{ \begin{smallmatrix} O \\ Cl^2 \end{smallmatrix} \right\}^{O^2}$
Triacetin . . .	$C^6H^{14}O^8$	$= C^3H^3O^3 + 3C^3H^4O^2$	$- 3H^2O = \left( \begin{smallmatrix} C^3H^3 \\ C^3H^4O^2 \end{smallmatrix} \right)^{''} \left\{ O^2 \right\}^{O^2}$
Triethylin . . .	$C^6H^{20}O^3$	$= C^3H^3O^3 + 3C^3H^4O$	$- 3H^2O = \left( \begin{smallmatrix} C^3H^3 \\ C^3H^4 \end{smallmatrix} \right)^{''} \left\{ O^3 \right\}^{O^2}$
Benzosuccinin . . .	$C^{14}H^{14}O^8$	$= C^3H^3O^3 + \left\{ \begin{smallmatrix} C^7H^8O^3 \\ C^7H^8O^4 \end{smallmatrix} \right\}$	$- 3H^2O = \left( \begin{smallmatrix} C^3H^3 \\ C^7H^8O^3 \\ C^7H^8O^4 \end{smallmatrix} \right)^{''} \left\{ O^2 \right\}^{O^2}$
Citrin . . .	$C^8H^{18}O^7$	$= C^3H^3O^3 + C^5H^8O^4$	$- 3H^2O = \left( \begin{smallmatrix} C^3H^3 \\ C^5H^8O^4 \end{smallmatrix} \right)^{''} \left\{ O^3 \right\}^{O^2}$
Acetodichlorhydrin . . .	$C^4H^8Cl^2O^3$	$= C^3H^3O^3 + \left\{ \begin{smallmatrix} C^2H^4O^2 \\ 2HCl \end{smallmatrix} \right\}$	$- 3H^2O = \left( \begin{smallmatrix} C^3H^3 \\ C^2H^4O^2 \\ C^2H^4O \end{smallmatrix} \right)^{''} \left\{ Cl^2 \right\}^{O^2}$
Trichlorhydrin . . .	$C^3H^3Cl^3$	$= C^3H^3O^3 + 3HCl$	$- 3H^2O = \left( C^3H^3 \right)^{''} \left\{ Cl^3 \right\}^{O^2}$
Dibromochlorhydrin . . .	$C^3H^3Br^2Cl$	$= C^3H^3O^3 + \left\{ \begin{smallmatrix} 2HBr \\ HCl \end{smallmatrix} \right\}$	$- 3H^2O = \left( C^3H^3 \right)^{''} \left\{ \begin{smallmatrix} Cl^2 \\ Br \end{smallmatrix} \right\}^{O^2}$

There is, however, a considerable number of glycerides, whose formation is attended with the elimination of a number of atoms of water greater or less than that which would be indicated by the rule above given, *e. g.* :

Epichlorhydrin . . .	$C^3H^3OCl$	$= C^3H^3O^2 + HCl - 2H^2O$
Epidichlorhydrin . . .	$C^3H^4Cl^2$	$= C^3H^3O^2 + 2HCl - 3H^2O$
Glycerotartaric acid . . .	$C^8H^{12}O^8$	$= C^3H^3O^3 + C^5H^8O^4 - H^2O$
Glycerotritartaric acid . . .	$C^{15}H^{22}O^{19}$	$= C^3H^3O^3 + 3C^5H^8O^4 - 2H^2O$

For additional examples, see the table given under ETHERS (p. 520).

These abnormal glycerides differ of course in atomicity from the normal glycerides, which are all triatomic. Those whose formation (like that of the third and fourth in the preceding table) is attended with the elimination of a number of water-atoms smaller than that required by the general rule are of higher atomicity than the normal glycerides (see the table, p. 520); these are for the most part of decided acid character. Those, on the contrary, which, like the first and second in the above table, eliminate in their formation a number of water-atoms greater than would be consistent with the formation of a normal glyceride, are of lower atomicity, and for the most part diatomic. They constitute a class of ethers called glycidic ethers, which may be derived from a hypothetical diatomic alcohol,  $\left( \begin{smallmatrix} C^3H^4 \\ H^2 \end{smallmatrix} \right)^{''} \left\{ O^2 \right\}$  or  $\left( \begin{smallmatrix} C^3H^3 \\ H \end{smallmatrix} \right)^{''} \left\{ O^2 \right\}$ , called glycide. This class of compounds includes the chlor- and bromhydrins which are distinguished in Berthelot's nomenclature by the prefix *epi*, and are produced from the triatomic chlorhydrins and bromhydrins by the action of alkalis. (See GLYCERIC ETHERS.)

*Occurrence and Formation of Glycerides.*—The normal glycerides containing acid radicles are artificially produced by acting upon glycerin with the corresponding acids, sometimes at ordinary temperatures, but more frequently with the aid of heat in sealed tubes, the particular compound formed depending upon the proportions of acid and glycerin present, the temperature to which the mixture is subjected, and the duration of the action. The chlorhydrins and bromhydrins are likewise produced by the action of the chlorides and bromides of phosphorus on glycerin.

The glycerides which are found in living vegetable and animal organisms all contain 3 at. of an acid radicle in place of the three replaceable hydrogen-atoms of glycerin. They are identical in all their properties with the triacid glycerides produced by artificial processes. Nearly all saponifiable fats are bodies of this nature, only a few yielding by this treatment alcohols different from glycerin, *e. g.* spermaceti, which yields ethal, or cetyllic alcohol, and Chinese wax, which yields ceryllic alcohol.

The glycerides which occur in plants in the form of oil or tallow are found chiefly in the seed, and most frequently in the testa, or seed-coating; rarely in the albumen (as in the poppy), or in the radicle, or in the fleshy matter surrounding the seed (as in the olive). *Cyperus esculentus* contains an oil in the root. In the animal body, fats are for the most part enclosed in the cellular tissue or in particular cavities.

Fats are separated from vegetable or animal tissue by pressure, at the temperature of the air, if they are sufficiently fluid; otherwise with the aid of heat; sometimes, however, the fat separates out spontaneously by simple fusion; or the fat may be dissolved out by boiling alcohol or ether, in which case it separates, sometimes by cooling, sometimes by evaporation, or on being mixed with water. The fat obtained by either of these processes is generally a mixture of several simple glycerides, which

may in some cases be separated, in consequence of their different fusibility, by pressing them at a temperature at which one is solid and the other liquid; thus the best kind of olive oil is obtained by filtering the crude oil at a temperature near the freezing point of water, only the most fluid portion then passing through. Another mode of separating fats is by taking advantage of their different degrees of solubility in alcohol and ether. But it is very difficult to obtain a perfectly pure simple glyceride by any of these processes.

*Properties.*—Glycerides in the solid state are white, transparent, or translucent. Some of them are crystalline, others have a close splintery fracture; specific gravity between 0.892 and 0.930. At a certain degree of cold they are brittle and friable, and at a less degree, more or less soft. Their melting-points range from 20 degrees or more below 0° C. to + 61° C. In the melted state they form viscid oils, generally colourless, sometimes yellowish or greenish, greasy to the touch, and making a permanent stain on paper. They are not volatile without decomposition, some only being capable of distillation in vacuo. They are neutral to vegetable colours, inodorous when pure, but often have a rancid odour, arising from incipient decomposition; they have little or no taste.

Glycerides are insoluble in water, sparingly soluble in alcohol, more soluble in ether: they dissolve also in sulphide of carbon. They mix readily with volatile oils; in the melted state they dissolve sulphur, phosphorus, and iodine (which however gradually decomposes them), also camphors, resins, and alkaloids. They are not soluble in aqueous ammonia, but liquid fats mix with it and form a white pasty mixture, called *liniment*, which takes a long time to separate.

Many glycerides are susceptible of isomeric modifications, differing in melting-point and other physical properties. Heintz observed that stearin from mutton fat, enclosed in a capillary tube and heated in a water-bath, becomes perfectly transparent at 51° or 52° C., opalescent at a somewhat higher temperature, resumes its opacity at 58°, and melts at 62–62.5°.

These phenomena have been more minutely examined by Duffy (Chem. Soc. Qu. J. v. 197) who finds that stearin is susceptible of three isomeric modifications, each distinguished by a particular melting-point. When gradually heated, it melts at the first of these points, viz. at about 51° C., then solidifies; melts at the temperature of the second, solidifies, melts at the temperature of the third (about 69°), and then solidifies only when the temperature has fallen below all three. After solidifying at this point, it may be made to melt again at the first, second, and third melting-points respectively, solidifying as before, below all three; and these changes are producible in this succession to any extent, without the slightest loss or gain of weight. As the stearin approaches to purity (by repeated crystallisation from ether), the interval between the first and second melting-points diminishes: hence it is probable that perfectly pure stearin\* (which has never yet been obtained) would exhibit only two melting points, those, namely, which are here called the first and third.

The three modifications also differ in density, the first being lighter, the second and third heavier than water; at 15°, the density of the first is 0.9867; of the second 1.0101, of the third 1.0178. These numbers apply to mutton-stearin crystallised 32 times from ether, and having its third melting point at 69.7°.

Similar modifications are exhibited by other glycerides, viz. stearin from beef-fat, a glycerin-fat from a kind of vegetable tallow (the history of which is not exactly known), palmitin and margarin. The following table exhibits the melting-points of these fats:

	Solidifying points.	Melting-points.		
		1	2	3
Mutton-stearin . . . . .	51.7° .	52.0° .	64.2°? .	69.7°
Beef-stearin . . . . .	50.5 .	51.0 .	63.0 .	67.0
Substance from vegetable tallow .	45.0 .	45.0 .	62.0 .	64.5
Palmitin from palm-oil . . . .	45.0 .	46.0 .	61.7 .	62.8
Margarin from butter . . . . .	40.0 .	40.5 .	51.0 .	52.6
Margarin (?) from human fat . .	43.5 .	44.2 .	54.5 .	56.0

The property of existing in two, if not three modifications, appears not to belong to any fatty substances excepting the glycerin-fats: at all events, the acids derived from them do not possess it; neither is it exhibited by stearic or cerotic ether, cerotin, cerotene, Chinese wax, or paraffin.

*Decompositions of Glycerides.*—1. *By distillation.*—Glycerides, which yield volatile acids, such as the acetics, butyrins, and valerins, may be more or less distilled without decomposition; but those which yield fixed acids, e. g. palmitin, olein, and stearin, are

\* The purest stearin which Duffy obtained had been crystallised 32 times from ether, and amounted to only 8 grammes from 2 kilogrammes of the crude fat; it still, however, appeared to be not quite pure; for the residue of the mother-liquor differed in melting point by 2° from that which crystallised out.



almost wholly decomposed by a heat of  $300^{\circ}\text{C}$ . and upwards, yielding numerous hydrocarbons, acrolein, with its products of decomposition (acrylic acid and acetic acid), more or less of the fatty acid contained in the glyceride, and a residue of charcoal, amounting to from 1 to 4 per cent. of the fat. When a fat is made to pass in drops through an iron tube at a low red heat, it yields but a small quantity of liquid products, but is for the most part resolved into a mixture of gases called *oil-gas*, possessing great illuminating power, and consisting of carbonic oxide, hydrogen, marsh gas, olefiant gas, the vapours of two empyreumatic oils (probably  $\text{C}^2\text{H}^2$  and  $\text{C}^3\text{H}^4$ ) and benzene,  $\text{C}^6\text{H}^6$ .

2. *By oxidation*.—Fats, in consequence of their higher boiling-points, require a stronger heat to set them on fire than the greater number of volatile oils. They burn with a very bright white flame, which deposits no soot unless the supply of air is insufficient.

Fats likewise undergo gradual oxidation by exposure to the air at ordinary temperatures. This change takes place most rapidly with fats which are liquid at the medium temperature of the air, and the fixed oils, when they thicken, turn rancid, and sometimes undergo spontaneous combustion. Fats of the stearin class, when pure, are but little changed by exposure to the air, but when mixed with oily fats, as generally happens, they exhibit alterations similar to the latter. Some fixed oils dry up by oxidation to an elastic resinous substance; others are converted into a thick greasy mass. Hence the distinction between *drying oils*, such as linseed oil, and *non-drying oils*, like rape and olive oils.

The thickening of fixed oils is purely an effect of oxidation; but the rancidity which many oils acquire by exposure to the air appears to depend in a great measure on the presence of certain azotised substances, such as gluten or cellular tissue, which putrefy on exposure to the air, and act as ferments in inducing a peculiar kind of decomposition. (See OILS.) Accordingly, animal oils are peculiarly subject to rancidity. Oils may be kept from turning rancid by Appert's process, that is, by placing bottles completely filled with them in water, keeping the water for some hours at the boiling heat, and closing the bottles tightly while the heating is continued.

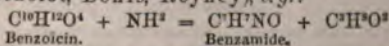
When porous substances, such as hemp or cotton, are saturated with fixed oils, so that the oil presents a very large surface to the air, the absorption of oxygen takes place more quickly; the development of heat which accompanies it accelerates the process; this again produces a more rapid evolution of heat, by which the oxidation is further accelerated; and at last, if the quantity of material is considerable, the temperature rises to the point at which rapid combustion takes place. This spontaneous combustion of fixed oils, which is a frequent cause of fires, takes place more readily with drying than with non-drying oils. It may take place in intervals varying from a few hours to several weeks, when considerable masses of lamp-black, tow, linen, paper, cotton, calico, woollen stuffs, ships' cables, wood-ashes, ochre, &c., are slightly soaked in oil and packed in such a manner that the air has moderate access to them. (See Graham's *Chemical Report on the Cause of the Fire in the Steamship "Amazon,"* Chem. Soc. Qu. J. v. 34.)

3. *Chlorine, bromine, and iodine* decompose fats, forming substitution-products, which have been but little examined.

4. Fuming *nitric acid* sets fire to drying oils. A mixture of this acid with strong sulphuric acid sets fire even to olein; but solid fats are but slowly decomposed by fuming nitric acid. When fats are heated for some time with dilute nitric acid, the products formed are the same as if a mixture of glycerin and the fatty acid had been similarly treated, the glycerin yielding oxalic, and perhaps also acetic acid, and the fatty acid being converted by progressive oxidation, first into a resinous mass, then into various other acids, such as suberic, pimelic, adipic, lipic, succinic acids, and others, differing according to the nature of the original acid. Olein yields, in addition to the acids above-mentioned, several volatile acids of the series  $\text{C}^n\text{H}^{2n}\text{O}^2$ , from acetic acid,  $\text{C}^2\text{H}^4\text{O}^2$ , to capric acid,  $\text{C}^{10}\text{H}^{20}\text{O}^2$ . When weak nitric acid acts for a short time only on fats, the oxidising action is exerted almost wholly on the glyceryl, the fatty acid being set free, occasionally in a somewhat altered state.

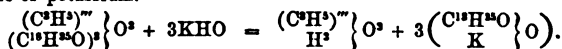
5. Strong *sulphuric acid*, at high temperatures, browns and blackens fats, giving off sulphurous and sometimes formic acid, and forming a resinous matter, a substance like tannin, and a coaly substance, all of which appear to contain sulphuric acid. Sulphuric acid, gently heated with twice its weight of fat, separates the fatty acid, and forms *sulphoglyceric acid*,  $\text{C}^3\text{H}^5\text{O}^3.\text{SO}^2$ .

6. Ammonia decomposes the glycerides into glycerin and the amide of the acid contained in them (Berthelot, Bonis, Royney), e.g.:



7. *Saponification*.—Glycerides, as already observed, are decomposed by caustic

*alkalis* and other hydrated oxides, yielding glycerin and a salt of the fatty acid, called a *soap*. Thus, when stearin is acted upon by caustic potash, the products are glycerin and stearate of potassium.



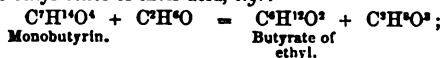
The stronger the base, the lower is the temperature at which the saponification may be effected. Caustic alkalis can saponify fats at ordinary temperatures, especially if the action be assisted by agitation; weaker bases, such as oxide of lead, also the alkaline carbonates, require a boiling heat, and water requires a very high temperature, such as can only be produced under increased pressure or by the use of superheated steam (p. 886).

At a temperature at which the tension of water-vapour is from five to six times that of the atmosphere, 4 pts. lime suffice to saponify completely 100 pts. fat in presence of water (Milly). One pt. lime-soap heated with an equal weight of water, and 40 times its weight of olive-oil, to 155° or 165° C., decomposes the oil completely. (Pelouze.)

Glycerides may also be saponified by *anhydrous oxides*, e.g. by lime, baryta, strontia, and oxide of lead. When tallow is heated with  $\frac{1}{10}$  or rather more of its weight of quicklime to about 250° C., the whole of the fatty acids contained in it are converted into lime-soaps, and the mass treated with water yields glycerin. During the saponification, water, acetone, and glycerin are given off, amounting to 2 or 3 per cent. of the tallow. (Pelouze, Compt. rend. xlii. 1001.)

When a glyceride is boiled with excess of alkali, the product is always a neutral soap, and if the quantity of alkali present is less than sufficient to neutralise the whole of the fatty acid present, part of the fat remains undecomposed. 100 pts. of hog's lard require for complete saponification 18 pts. of hydrate of potassium, the product then consisting of neutral stearate, oleate, &c., of potassium, without excess of either acid or alkali; but, if 100 pts. of lard are boiled for 60 hours with 9 pts. of hydrate of potassium and a small quantity of water, a homogeneous mass is obtained, consisting of neutral stearate, &c. of potassium, mixed with half the fat in its original state. The mixture thus formed is almost wholly soluble in alcohol, and does not form grease-spots, a property on which the power of soap to remove grease-spots chiefly depends. The same mixture, boiled with a large quantity of water, is decomposed into soluble soap and unaltered fat. (Chevreul.)

Some glycerides are decomposed when heated with *alcohol* in sealed tubes, yielding glycerin, and the ethyl-ether of their acid, e.g.:



but most glycerides are thus decomposed only when an acid, such as hydrochloric acid, is present, or a quantity of alkali not sufficient to neutralise the whole of the fatty acid (Berthelot); e.g.:



A simple fat, when saponified, yields glycerin and only one acid; but if the fat is a mixture of several glycerides, which is generally the case with natural fats, each of these yields a peculiar acid; so that, for every acid yielded by a fatty mixture, a corresponding glyceride may be supposed to exist therein.

To ascertain what acids have been obtained by the saponification of a fat, the first thing to be done is to decompose all the soap-salts with dilute sulphuric acid, and then separate the volatile from the fixed acids by distillation. The several volatile acids in the distillate may then be further separated by fractional distillation; acetic, butyric, and valeric acids, better by Liebig's method of partial saturation with potash, and subsequent distillation (i. 250).

To separate the fixed acids, Heintz (Pogg. Ann. lxxxiv. 221) dissolves the mixture in such a quantity of alcohol, that nothing separates out from the solution at 0° C., and adds to the boiling alcoholic solution a quantity of acetate of lead sufficient to convert about half the acids into lead-salts, the quantity of the crystallised acetate required for this purpose being generally about one-third of the weight of the acid mixture. Any precipitate which forms at the boiling heat is to be redissolved by a few drops of acetic acid, and the solution left to cool. The liquid is then filtered from the salts, which separate in the solid state, by filtration and pressure, and the fatty acids are separated from both the dissolved and the solid lead-salts by sulphuric acid. The fractional precipitation is then to be repeated in the same manner in both portions of acid, till the products no longer exhibit any alteration of melting-point or other physical properties. [For Chevreul's method of separation, see his "Recherches sur les corps gras;" also Gm. vii. 233.] The separation of the fatty

acids is on the whole a less difficult problem than that of the fats themselves; indeed, the only way of obtaining an absolutely pure glyceride is to produce it artificially by the action of the corresponding acid upon glycerin.

The following is a list of the fatty acids which have been obtained from natural glycerides:

1. Volatile acids.		2. Fixed acids.	
Butyric	. . . . . $C^4H^8O^2$	Laurostearic	. . . . . $C^{18}H^{36}O^2$
Valeric	. . . . . $C^5H^{10}O^2$	Cocinic	. . . . . $C^{18}H^{36}O^2$
Caproic	. . . . . $C^6H^{12}O^2$	Myristic	. . . . . $C^{18}H^{36}O^2$
Caprylic	. . . . . $C^8H^{16}O^2$	Benic?	. . . . . $C^{18}H^{36}O^2$
Capric	. . . . . $C^{10}H^{20}O^2$	Moringic	. . . . . $C^{18}H^{36}O^2$
Hercic	. . . . . ?	Linoleic	. . . . . $C^{18}H^{36}O^2$
Sabadillie	. . . . . ?	Palmitic	. . . . . $C^{18}H^{36}O^2$
Crotonic	. . . . . $C^4H^8O^2$	Hypogaic	. . . . . $C^{18}H^{36}O^2$
Ricinic	. . . . . ?	Margaric	. . . . . $C^{18}H^{36}O^2$
		Oleic, Elaidic, and Ricinoleic	$C^{18}H^{36}O^2$
		Stearic	. . . . . $C^{18}H^{36}O^2$
		Arachidic	. . . . . $C^{20}H^{40}O^2$

According to Heintz, margaric acid is merely a mixture of stearic and palmitic acids; and benic acid is identical with palmitic acid.

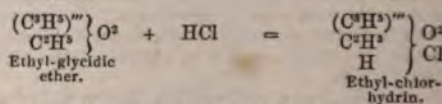
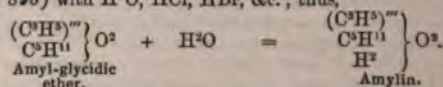
The neutral fats corresponding to several of these acids have not been obtained in the separate state, their existence being merely inferred from the formation of corresponding acids in the saponification of mixed fats.

The normal glycerides containing acid radicles are specially described after the several acids (see ACETINS, BUTYRINS, CHLORHYDRINS, &c.). The acid glycerides (glycerophosphoric acid, &c.) and the glycidic ethers (p. 895) will be described in separate articles. We shall here describe the normal glycerides containing monatomic alcohol-radicles, of which the following have been prepared and analysed by Reboul (Ann. Ch. Phys. [3] lx. 5; Jahresb. d. Chem. 1860, p. 462), and by Reboul and Lourenço. (Compt. rend. lii. 466; Jahresb. 1861, p. 674.)

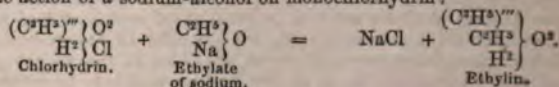
*Glycerides containing Monatomic Alcohol-radicles.*

Ethylin	. . . . . $C^2H^4O^2$	=	$C^2H^4(C^2H^4)O^2$
Amylin	. . . . . $C^5H^{10}O^2$	=	$C^5H^7(C^5H^{11})O^2$
Ethylchlorhydrin	. . . . . $C^2H^4ClO^2$	=	$C^2H^4(C^2H^4)ClO^2$
Amylchlorhydrin	. . . . . $C^5H^{10}ClO^2$	=	$C^5H^7(C^5H^{11})ClO^2$
Diethylin	. . . . . $C^4H^8O^2$	=	$C^4H^8(C^2H^4)^2O^2$
Ethylamylin	. . . . . $C^7H^{14}O^2$	=	$C^7H^9(C^2H^4)(C^5H^{11})O^2$
Diamylin	. . . . . $C^10H^{20}O^2$	=	$C^10H^{15}(C^5H^{11})^2O^2$
Diethylchlorhydrin	. . . . . $C^4H^8ClO^2$	=	$C^4H^8(C^2H^4)^2ClO^2$
Ethyl-chlorobromhydrin	. . . . . $C^2H^4BrClO$	=	$C^2H^4(C^2H^4)BrClO$
Triethylin	. . . . . $C^6H^{12}O^2$	=	$C^6H^9(C^2H^4)^3O^2$

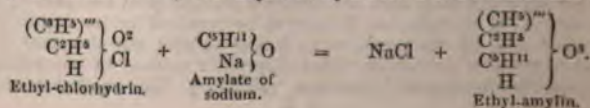
The glycerin-ethers containing 1 at. of a monatomic alcohol-radicle are produced: 1. By the combination of a glycidic ether containing a monatomic alcohol-radicle (p. 895) with  $H^2O$ ,  $HCl$ ,  $HBr$ , &c.; thus,



2. By the action of a sodium-alcohol on monochlorhydrin:

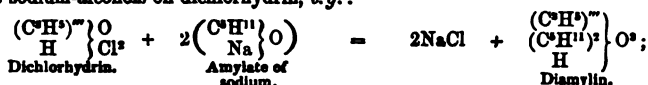


Glycerin-ethers containing 2 at. of a monatomic alcohol-radicle are produced by the action of ethyl- or amyl-chlorhydrin on a sodium-alcohol: thus,

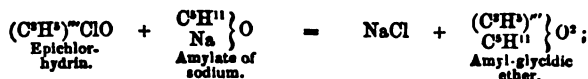




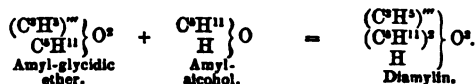
Diethylin and diamylin are however more conveniently prepared by the action of the sodium-alcohols on dichlorhydrin, *e. g.*:



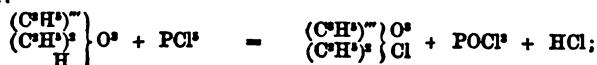
or on epichlorhydrin, in which case it is probable that a glycidic ether is first formed, *e. g.*:



and this, uniting with the free alcohol usually present in the sodium-alcohol, forms the glycerin-ether:



Diethylechlorhydrin is produced by the action of pentachloride of phosphorus on diethylin:



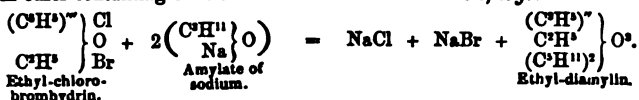
and this compound, treated with ethylate of sodium, forms triethylin:



Triethylin may also be obtained, though less pure, by the action of iodide of ethyl on the sodium-salt of diethylin:



The methods above described for the preparation of the ethyl- and amyl-derivatives of glycerin are evidently of general application. Another general method of preparing the glycerides in which all three atoms of the typic hydrogen are replaced by alcohol-radicles, is to treat a sodium-alcohol with the compound resulting from the union of a glycidic ether with an ordinary monatomic ether: thus epichlorhydrin,  $\text{C}^2\text{H}^5\text{ClO}$ , heated in a sealed tube with bromide of ethyl,  $\text{C}^2\text{H}^5\text{Br}$ , forms ethylechlorobromhydrin,  $\begin{array}{c} (\text{C}^2\text{H}^5)^m \\ \text{C}^2\text{H}^5 \end{array} \left\{ \text{Cl} \right\} \text{O}^s$ ; and this compound treated with 2 at. of a sodium-alcohol yields a glycerin-ether containing 3 at. of a monatomic alcohol-radicle, *e. g.*:



**Ethylin**,  $\text{C}^2\text{H}^{10}\text{O}^s$ .—Obtained by adding chlorhydrin to ethylate of sodium, heating the resulting mass to  $200^\circ \text{C}$ . to expel the excess of alcohol, treating the residue with water, and then with carbonate of potassium, agitating with ether, evaporating the ethereal solution over the water-bath, and submitting the residue to repeated fractional distillation. It is an oily liquid, boiling between  $226^\circ$  and  $230^\circ \text{C}$ ., soluble in water, and precipitated therefrom by carbonate of potassium. (Reboul.)

**Ethyl-chlorhydrin**,  $\text{C}^2\text{H}^{11}\text{ClO}^s$ , obtained by agitating ethyl-glycidic ether with fuming hydrochloric acid, is a combustible liquid, having a pungent peppery odour, boiling at  $180^\circ \text{C}$ ., insoluble in water, somewhat soluble in hydrochloric acid. (Reboul.)

**Diethylin**,  $\text{C}^4\text{H}^{10}\text{O}^s$ , obtained by the action of ethylate of sodium on dichlorhydrin, is a liquid whose vapour-density is by observation = 5.22; by calculation (2 vol.) = 5.14. (Reboul.)

**Diethylechlorhydrin**,  $\text{C}^4\text{H}^{12}\text{ClO}^s$ , is a liquid of specific gravity 1.005 at  $17^\circ \text{C}$ .; insoluble in water, miscible with alcohol and ether.

**Ethylechlorobromhydrin**,  $\text{C}^4\text{H}^{12}\text{BrClO}$ , is a heavy oily liquid boiling between  $186^\circ$  and  $188^\circ$ , insoluble in water, but soluble in all proportions in alcohol and ether. Obtained by heating epichlorhydrin with bromide of ethyl.

*Triethylin*,  $C^3H^3O^3$ , obtained by heating diethylechlorhydrin with ethylate of sodium to  $120^\circ C.$ , evaporating the excess of alcohol over the water-bath, and treating the residue with water, is a colourless oil, boiling between  $180^\circ$  and  $190^\circ C.$ , insoluble in water, soluble in alcohol and ether.

*Amylin*,  $C^8H^{10}O^3$ .—Reboul obtained this compound by heating amyl-glycidic ether with water to  $200^\circ C.$  in a sealed tube for several hours;  $\left\{ \begin{smallmatrix} C^2H^3 \\ C^2H^3 \end{smallmatrix} \right\} O^2 + H^2O = C^8H^{10}O^3$ . Two layers then form, the upper of which, when agitated with aqueous carbonate of potassium, to remove water, then distilled and repeatedly rectified, yields amylin as a colourless, thickish liquid, of specific gravity 0.98 at  $20^\circ C.$  It burns with a bright flame; boils between  $260$  and  $262^\circ C.$ ; is soluble in water, 1 volume of it mixing with 2 vol. water, but not with more; and mixes in all proportions with ether.

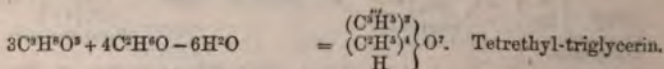
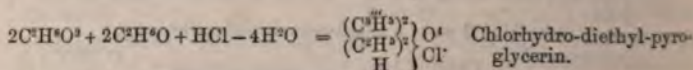
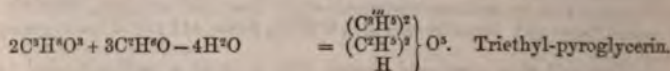
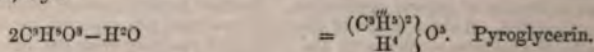
*Amyl-chlorhydrin*,  $C^8H^{11}ClO^2 = C^8H^9(C^2H^3)ClO^2$ , obtained by agitating amyl-glycidic ether with fuming hydrochloric acid, is an oily liquid of specific gravity 1.0 at  $20^\circ C.$ , boiling at  $235^\circ$ , insoluble in water. (Reboul.)

*Amyl-bromhydrin* and *Amyl-iodhydrin* are obtained in like manner. The latter, which is produced with violent action, is a heavy liquid having a repulsive odour, and not volatile without decomposition. (Reboul.)

*Diamylin*  $C^{10}H^{12}O^3 = C^8H^9(C^2H^3)^2O^3$ , obtained by treating dichlorhydrin with amylate of sodium, dissolving out the resulting chloride of sodium with water, distilling the liquid which rises to the surface, and rectifying the portion which goes over between  $275^\circ$  and  $290^\circ C.$ , is a strong-smelling liquid, of specific gravity 0.907 at  $9^\circ C.$ , boiling between  $272^\circ$  and  $274^\circ$ , insoluble in water, not attacked by potash. Heated with hydrochloric acid to  $100^\circ C.$  in closed vessels, it yields chloride of amyl. (Reboul.)

*Ethylamylin*,  $C^{10}H^{12}O^3 = C^8H^9(C^2H^3)(C^2H^3)O^3$ , prepared in like manner by the action of amylchlorhydrin on ethylate of sodium, is a liquid of specific gravity 0.92, boiling between  $238^\circ$  and  $240^\circ C.$ ; burning with a bright flame, insoluble in water.

**Polyglycerides.** These are glycerides derived from 2 or more molecules of glycerin, either by simple dehydration in various degrees, or by dehydration and the replacement of the whole or part of the remaining typic hydrogen by acid or alcohol-radicles, e.g.:



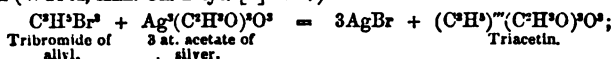
For the special description of these compounds see GLYCERYL, HYDRATES OF (p. 893).

**GLYCERIN.**  $C^3H^5O^3 = \left\{ \begin{smallmatrix} C^2H^3 \\ H^1 \end{smallmatrix} \right\} O^2 = (C^2H^3)^2.(HO)^2$ . *Principe doux des huiles, Oelsüss, Oelzucker.* (Gm. ix. 486.—xiii. 666; Gerh. i. 763; iv. 912.)—This substance is produced from most of the fixed oils and solid fats existing in the bodies of plants and animals by the process of saponification, that is to say, by treating these fatty bodies with an alkali, or other metallic oxide, in presence of water, or with water itself at a high temperature. It does not, for the most part, exist ready formed in natural fats, but is formed from them, together with a fatty acid, by addition of the elements of water, just as alcohol may be produced from acetate of ethyl. In short, glycerin is an alcohol, and bears to the fats, stearin, olein, &c., the same relation that alcohol bears to the compound ethers. (See ALCOHOLS, ETHERS, and GLYCERIDES.) It was discovered in 1779 by Scheele, who obtained it in the preparation of lead-plaster by saponifying lard with oxide of lead. Chevreul (*Recherches sur les corps gras d'origine animale*, 1823) afterwards showed that it is a constant product of the saponification of the ordinary fats, and pointed out the relations just mentioned; and the recent researches of Berthelot (Ann. Ch. Phys. [3] xli. 216) on the synthesis of fats by the

direct action of acids upon glycerin, have shown that this body is a triatomic alcohol, in which 1, 2 or 3 at. of hydrogen may be replaced by acid radicles, producing fatty or oily compounds, some of which are identical in composition and properties with the natural fats, stearin, palmitin, &c.

Glycerin exists ready formed in a few vegetable oils, in palm-oil for example, from which it may be obtained by simple treatment with boiling water. Pasteur has shown that it is always produced in the alcoholic fermentation of sugar, to the amount of about 3 per cent. of the sugar decomposed, and that it occurs in all fermented liquors, especially in wine. (Compt. rend. xlv. 557; xlvii. 224.)

*Artificial Formation.*—Tribromide of allyl heated with acetate of silver yields triacetin, and triacetin treated with caustic alkalis, baryta-water for example, yields glycerin (Wurtz, Ann. Ch. Phys. [3] li. 97):



and



This reaction does not, however, afford the means of synthetically forming glycerin from inorganic constituents: for tribromide of allyl has hitherto been obtained only from iodide of allyl (iodotriethylene), which in its turn is obtained from glycerin itself. The process is therefore more strictly analogous to the formation of glycerin by ordinary saponification than to a true synthesis.

*Preparation.*—1. *By saponification with oxide of lead.*—Five pts. of finely pounded litharge are heated with nine pts. of olive oil or any other glyceride and a small quantity of water, the mixture being stirred, and the water renewed till the oxide of lead is converted into a plaster; the watery liquid is then separated from this plaster, and freed from lead by a stream of sulphydric acid gas, and the filtrate is evaporated to a syrup over the water-bath.

For many years all the glycerin of commerce was obtained by this method; but it was very apt to retain small quantities of lead, the presence of which is very objectionable in any therapeutic application of glycerin.

2. *From the alkaline mother-liquor of the soap-works* (from which the soap has been separated by means of common salt), by neutralising with sulphuric acid; removing the excess of that acid by carbonate of barium; evaporating the filtrate to a syrup; digesting it for several days with alcohol; separating the alcoholic liquid from the sulphate of sodium which crystallises out; decolorising with animal charcoal; again evaporating to a syrup; exhausting the residue with strong alcohol; and finally evaporating the filtered solution over the water-bath (Riegel). This process is, however, too troublesome and expensive for use on the large scale.

The separation of glycerin from spent soap-lyes may be more economically effected by means of superheated steam, a method of doing which has been patented by H. Reynolds (10th of June, 1858). The liquid may be first reduced by evaporation, and raised nearly to the boiling point, by being passed through a heated still-like vessel, or heated in any other convenient vessel. It is then passed into a second vessel, where it is met by a jet or jets of superheated steam, at a temperature of 350° to 400° Fahr., which raises it to the boiling point and evaporates the glycerin, carrying the vapour upwards with it, and leaving the salts to deposit in the vessel. If greater purity is required, it may be obtained by repeating the process, and the little colour that remains can easily be removed by animal charcoal or chlorine.

3. *From the residue of the manufacture of stearic acid for candles.*—In this process tallow is saponified by lime, and the glycerin separates from the calcium-salts of the fatty acids in the form of a brown liquid, which may be purified by evaporating to a syrup, treating the residue with alcohol as above, expelling the alcohol from the filtered liquid by distillation, digesting the solution with oxide of lead, till a portion of the oxide is dissolved, then filtering and removing the lead by sulphydric acid. The object of this treatment is to free the glycerin from a peculiar acid which is produced during the saponification, and forms with lead an insoluble basic salt. The liquid, after being treated with sulphydric acid, has merely a slight yellowish tint, which may be completely removed by animal charcoal. It is then concentrated by evaporation.

A process better adapted for preparation on the large scale is that of M. Cap. The liquid containing the glycerin from lime-saponification is concentrated, and afterwards treated with sulphuric acid to remove the remaining lime. It is then boiled and agitated in a close vessel to expel volatile fatty acids, left to cool when it has attained the density of 1.07 (14° of Twaddell's hydrometer), then rendered neutral, if necessary, by the



addition of carbonate of lime. After this the boiling is renewed, and continued till the liquid marks  $37.5^{\circ}$  Tw. (specific gravity 1.187), when it is again cooled, and any further deposit of sulphate of lime removed by filtration. Finally, the liquid is concentrated by evaporation to  $49^{\circ}$  Tw. (specific gravity 1.245), and passed through washed animal charcoal to remove the colour. This reduces the density to  $45^{\circ}$  Tw. (specific gravity 1.225), but by careful concentration, a fourth part of the water may be removed, and the density raised to  $51.2^{\circ}$  (specific gravity 1.256).

This method, when properly carried out, yields a very pure product, but it is somewhat complicated, and unless great attention is paid to every part of it, small quantities of lime are apt to remain in the glycerin, rendering it unfit for many purposes, especially for use in medicine and pharmacy.

3. *By heating neutral fats with water or with steam.*—This is the only unobjectionable method of obtaining glycerin, inasmuch as it alone ensures the entire absence of mineral impurities. It was first carried out by Mr. Tilghman in the following manner. The fat or oil having been thoroughly mixed to an emulsion with about half its bulk of warm water, is forced by a pump through a long coil of strong iron tubing heated to about the temperature of melted lead, the pump being worked at such a rate that the liquid may occupy about ten minutes in travelling through the coil. On issuing from the coil, the liquid separates into two layers, the upper of which consists of the fatty acid, and the lower of an aqueous solution of glycerin, which requires only to be concentrated by evaporation.

This process is very simple, and is capable of yielding very pure products. It has not, however, been carried out on a very large scale in the form just described, but it appears to have led to the invention of the method by which nearly all the pure glycerin of commerce is now obtained, viz. the decomposition of the fats by distillation in an atmosphere of superheated steam.

The distillation of fatty bodies and the introduction of steam into the apparatus was first suggested by Chevreul and Gay-Lussac, in 1825, and the process was afterwards carried out, with various improvements and modifications, by several chemists and manufacturers, both in this country and in France. But all these processes had for their special object the preparation and purification of the fat acids, not of the glycerin; indeed, the temperature employed was generally so high that the glycerin was completely decomposed, giving off intensely acid fumes of acrolein, and leaving a charred residue. The distillation of fats in an atmosphere of steam in such a manner as to obtain the glycerin as well as the fatty acids, was first effected by the process above-mentioned, patented by G. F. Wilson and G. Payne on the 24th of July, 1854. The process is as follows:

An ordinary still and condensing or refrigerating apparatus is employed, preference being given to one with an ample refrigerating surface. The bottom of the still is heated by a fire provided with a damper to the flue or chimney, that the contents may not be heated above the desired temperature. In charging a still, a quantity of neutral or partially neutral fats is introduced into the heated still, and heated steam is introduced below the fats or oils, so as to rise up through them in numerous streams, care being taken that the temperature of the matters in the still shall not rise to the temperature which will decompose the glycerin. A thermometer is inserted into the still to indicate the temperature of the contents, and it is desirable in all cases with neutral fats and oils, to keep the heat below  $600^{\circ}$  and above  $550^{\circ}$  Fahr.; the glycerin is then not decomposed, but comes over very pure. When the fats or oils are only partially neutral, which is very commonly the case with palm-oil, the draught of the fires may be quickened, and the process hastened so long as there are fat acids in the still; but as soon as the fat acids have passed over, if the temperature is much above  $600^{\circ}$  Fahr., acrolein will probably be formed, particularly if steam be not freely supplied, its production being quickly indicated by its pungent smell, and its action on the eyes of persons near the condenser. Charges have nevertheless been worked off at higher temperatures, keeping up a very plentiful supply of steam, and the glycerin has not been decomposed; still, there is no superior result obtained, whilst there is greater hazard of decomposing the glycerin.

It is, however, most convenient to retain the contents of the still rather under than above  $600^{\circ}$  Fahr. (keeping up a free supply of steam) during the whole process, whether the fats or oils be neutral or partially neutral. The external heat immediately under the still should be very moderate, the heated steam admitted into the still being chiefly depended on for maintaining the higher temperature. Different neutral fatty and oily substances appear to vary in some degree, but not to a great extent, in regard to the temperature at which they may be distilled most quickly in an atmosphere of steam without decomposing the glycerin.

When a still with a refrigerator or condenser in successive compartments is used, each provided with a cock to draw off the distilled and condensed products, which is the

most convenient arrangement, it is found that the products which flow from the hottest of the condensers are for the most part free from water and glycerin, the greater part of the glycerin passing off with the products which condense in the compartments of the condenser more distant from the still, where the temperature is lower; and in all the receivers, the fat acids quickly separate from the glycerin and water, when allowed to stand and cool for a short time. The compartment of the condenser most distant from the still is open to the atmosphere, no pressure being necessary within the still and condenser.

When the glycerin is required in a more concentrated state than it is when it comes over and is condensed, the water contained in it may be more or less separated by evaporation.

The process of distillation just described may also be employed to purify glycerin prepared by either of the old processes, such as saponification by lime or oxide of lead.

For the description of various forms of apparatus for distilling fats with superheated steam, see *Richardson and Watts's Chemical Technology*, i. part 3, p. 754.

4. Lastly, glycerin may be separated from fats by the action of *hydrochloric acid*. When castor-oil is dissolved in absolute alcohol, and hydrochloric acid gas is passed through the heated solution for some time, and the liquid is agitated with water, an aqueous solution of glycerin is obtained, surmounted by an oily liquid. On decanting the watery liquid with a siphon, evaporating to a syrup, and treating the residue with ether, that liquid dissolves out the fatty acids of the castor-oil, and leaves the glycerin. (Rochleder, *Ann. Ch. Pharm.* lix. 260.)

*Properties.*—Glycerin, concentrated as much as possible by evaporation, is an uncrystallisable syrupy liquid, colourless, inodorous, sweet to the taste, neutral to test-paper. Its specific gravity is 1.260 at 15.5° C. (60° F.) When it is distilled *per se*, only a small portion passes off undecomposed, but in an atmosphere of steam it distils without decomposition.

Glycerin dissolves in *water* in all proportions. The following table exhibits the specific gravities and freezing points of aqueous solutions containing different percentages by weight of glycerin.

Glycerin per cent.	Specific gravity.	Freezing point.	Glycerin per cent.	Specific gravity.	Freezing point.
10	1.024	-1° C.	60	1.169	} below -35° C.
20	1.051	-2.5°	70	1.179	
30	1.076	-6°	80	1.120	
40	1.105	-17.5°	90	1.232	
50	1.127	-31.34°	94	1.241	

When an aqueous solution of glycerin freezes, only a portion of the water passes into the solid state, while a more concentrated solution of glycerin still remains liquid. (Fabian, *Dingl. pol. J.* clv. 345.)

Glycerin dissolves also in all proportions in *alcohol* and in *chloroform*, but is insoluble in *ether*.

Glycerin dissolves *iodine* in large quantity, forming an orange-yellow solution, without decomposition. Aqueous glycerin dissolves *arsenious acid* more abundantly than pure water, the solution depositing part of the acid on standing, and more quickly when boiled. (Schiff, *Ann. Ch. Pharm.* cxviii. 86.)

With *baryte*, *strontia*, and *lime*, glycerin forms compounds soluble in water and not precipitated by carbonic acid. Even in the anhydrous state, it dissolves considerable quantities of *potash* and *soda*. It dissolves all *deliquescent salts*, and many others, e.g. the *sulphates of potassium, sodium, and copper*, the *chlorides of potassium and sodium*, &c. Aqueous and even anhydrous glycerin dissolves *oxide of lead*, and consequently does not precipitate a solution of basic acetate of lead. Other bodies, insoluble in water, are not dissolved by anhydrous glycerin (Pelouze). *Sesquichloride of iron* mixed with a large quantity of glycerin is not precipitated by alkalis or alkaline sulphides (H. Rose). *Sulphate of copper* mixed with glycerin forms, with a small quantity of potash, a precipitate which dissolves in excess of potash; but the resulting blue solution decomposes below 100° C., depositing bluish flakes.

Glycerin dissolves the *vegetable acids*, and dissolves or suspends the *vegetable alkalis* in the same manner as aqueous liquids, the resulting products being available for the same purposes as though mixed with oil. Thus the salts of *morphine* dissolve in it completely, even cold, in all proportions. *Sulphate of quinine*, in the proportion of one-tenth, dissolves in it when hot, but when cold, separates in clots, which, when



trituated with the supernatant liquid, give it the consistence of a cerate, very useful for frictions and embrocations. It is the same with the salts of *brucine*, *strychnine*, *veratrine*, and most preparations of the same order.

*Uses.*—The solvent powers of glycerin, its unctuous character, and its property of remaining liquid even at low temperatures, together with its perfect harmlessness, render it a valuable agent in pharmacy, as an excipient for various substances, and for many other purposes, as in the preparation of cosmetics. It is used also for mixing with soap, forming the "glycerin-soap" recommended for softening the skin. It has been found very useful as an outward application in skin-diseases and inflammations of the mucous membranes of the nose, mouth, &c., and has been used in diseases of the eye and ear, and as a substitute for cod-liver oil in the treatment of phthisis; but its efficacy in these latter cases is not yet satisfactorily proved.

Glycerin may also be used for preserving articles of food, especially those which require to be kept moist, as sugar, fruits, chocolate, &c., enclosed in tin cases. Meat keeps well in it, retaining its flavour and softness. A very useful application of it is to mix with tobacco for the purpose of keeping it moist.

Barreswil recommends the use of glycerin for keeping modelling clay moist. It is also useful as a solvent for gum-arabic and white of egg, the solutions remaining unaltered for a long time, and for *aniline-violet* (*aniline* or *indisine*); the solubility of this colouring matter in glycerin has not been exactly ascertained, but it appears to dissolve more freely in that liquid than in alcohol or acetic acid. (C. Gros-Renaud, *Rép. Chim. app.*, 1859, p. 427.)

Amadon (*Technologiste*, January 1858, p. 191), describes a process of madder-dyeing with the aid of glycerin. Alizarin and alcoholic madder-extract dissolve in glycerin even in the cold; at higher temperatures more quickly and in larger quantity, so that the liquid acquires a deep scarlet colour. The alcoholic extract of madder does not yield any deposit on cooling, or on addition of water, but the solution of alizarin in glycerin deposits red flocks on being mixed with water.

Messrs. Vasseurs and Houbigant have patented (May 21, 1856), the application of glycerin for the preparation of ink, paper, and other materials. Glycerin diluted with four or five times its weight of water, imparts to paper the peculiarity of retaining a permanently damp condition, so that, in taking copies of letters, &c., written on paper so prepared, pressure and damping of the copying paper will not be required. The writing paper may be prepared either by introducing glycerin into the pulp of which it is to be manufactured, or by damping it therewith after it has been made up into books or otherwise. Or, ink may be prepared or combined with glycerin, and writings effected with the ink so treated will remain for a long period in a sufficiently damp state to allow of copies or impressions being taken without pressure or damping of the copying paper.

Glycerin may also be employed, instead of common salt, for preserving untanned skins and hides, especially when intended for exportation, and therefore requiring rapid means of applying a preserving agent. Paste, cement, mortar, mastic, and other matters, especially when intended for daily use, may be treated with glycerin, in order to keep them in a suitably damp condition; this treatment will also have the effect of preserving them from frost. Vesicatory or blister paper, lint, and textile fabrics, particularly cloths, rags, and bandages, intended for medical, or surgical purposes, may be treated with glycerin to render them absorbent.

As glycerin never freezes, and is not altered by exposure to the air, it may be advantageously applied as a lubricator for delicate machinery, such as clockwork. For this purpose it is superior to the purest olein or oleic acid, the lubricants commonly used, as the former thickens by oxidation, and the latter solidifies at a few degrees below the freezing point of water. It may also be added to the water of gas-meters to prevent freezing and evaporation. The introduction of a few drops of it into the tube of a mercurial pressure-gauge is said to prevent the mercury from sticking to the surface of the glass, and thus enable it to record the pressure more exactly. (Friedheim, *Dingl. pol. J.* clxvi. 237.)

Lastly, it is well adapted for filling the *floating compasses* used on board screw-steamers, being preferable for that purpose to water, alcohol, or fluid-tar, the liquids hitherto employed, because it neither solidifies in cold, nor evaporates in hot climates. (Santi, *Compt. rend.* li. 1093.)

*Impurities and Adulterations.*—Glycerin prepared by the older methods (1 and 3, p. 876) is apt to be contaminated with small quantities of lead or lime. The former may be detected by sulphydric acid; the latter by dissolving the glycerin in its own volume of alcohol containing 1 per cent. of sulphuric acid, in which case, if lime is present, a precipitate will be formed. (Cap, *J. Pharm.* [3] xxv. 81.)

Glycerin prepared by distillation is free from these and all other mineral impurities; but the great extension which has of late years been given to the industrial applications

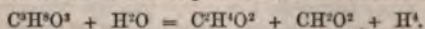


of this compound has led to the practice of adulterating it with various kinds of sugar. This adulteration, even if it amounts to three-fourths of the entire liquid, is not easily detected by ordinary observation, since the sugar does not alter either the taste or the syrupy character of the glycerin; but it may always be discovered, whatever the kind of sugar employed for adulteration, by examining the liquid with polarised light, inasmuch as all kinds of sugar (excepting mannite, which is too costly for the purpose) turn the plane of polarisation either to the right or to the left, whereas glycerin is totally destitute of optical rotatory power. The only kinds of sugar likely to be used for adulterating glycerin are cane-sugar, starch-sugar, and syrups containing uncrystallisable sugar (p. 864). The two former of these sugars turn the plane of polarisation to the right, though in different degrees; the third turns it to the left; moreover cane-sugar when boiled for about ten minutes with one-tenth of its volume of strong hydrochloric acid, is *inverted*, that is, converted into *lævo*-rotatory, uncrystallisable sugar (p. 864), whereas starch-sugar (dextroglucose) remains unaltered when thus treated. The direction of the rotatory power possessed by the solution before and after treatment with hydrochloric acid, serves therefore to distinguish between these two kinds of sugar. The optical method serves also to determine the quantity of either kind of sugar used to adulterate the glycerin; but for the mode of applying it for this purpose, we must refer to the article SACCCHARIMETRY.

Another method of detecting and estimating either kind of sugar in glycerin is by means of *chloroform*, in which glycerin dissolves with ease, whereas cane-sugar and glucose are quite insoluble. The liquid is first heated to expel the water contained in it, then mixed with chloroform; the whole is then poured upon a tared filter, and repeatedly washed with chloroform, after which the filter with its contents is dried at 100° C. and weighed. (Palm, Zeitschr. anal. Chem. 1862, p. 486.)

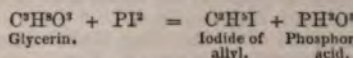
The presence of glucose may also be detected by boiling the liquid with caustic *potash* or *soda*: if glucose is present, a brown colour will be produced, whereas glycerin, either pure or adulterated only with cane-sugar, will not produce this colour (Cap; Palm). According to Palm, the presence of cane-sugar may be detected by adding a drop or two of *dilute sulphuric acid*, and heating the liquid in the water-bath till all the water is expelled; if cane-sugar is present, the liquid ultimately blackens, an effect which is not produced by glycerin, either pure or containing only glucose.

*Decompositions*.—1. Glycerin distilled *per se* passes over partly unaltered; but the greater portion suffers decomposition, yielding acrolein, acetic acid, empyreumatic oil, combustible gas, and carbonic anhydride, together with polyglyceric compounds (p. 894).—2. Distilled with *phosphoric anhydride*, it yields a distillate of pure acrolein ( $C^3H^4O = C^3H^4O^2 - 2H^2O$ ).—3. Distilled with *acid sulphate of potassium*, it also yields acrolein, but mixed with acrylic acid and other secondary products, likewise giving off sulphurous anhydride, and leaving a carbonaceous residue.—4. With free access of air, glycerin *burns* with a clear flame like an oil.—5. Anhydrous or nearly anhydrous glycerin in contact with *platinum-black*, becomes heated, gives off a slightly acid vapour, and, according to Döbereiner, is converted into a non-volatile, uncrystallisable acid, which, with aid of heat, reduces mercurous nitrate and nitrate of silver. If the experiment be made in oxygen gas over mercury, complete absorption takes place in a few hours, the same acid is formed, but is ultimately converted into water and carbonic anhydride.—6. When the aqueous solution of glycerin is evaporated in contact with the *air*, a brown substance is formed which is precipitated by basic acetate of lead.—7. Glycerin is rapidly decomposed by *peroxide of manganese* and *hydrochloric* or *sulphuric acid*, yielding carbonic anhydride and a large quantity of formic acid.—8. Glycerin is oxidised by *nitric acid*, the nature of the products varying according to the manner in which the action takes place. If it be moderated by external cooling, and by carefully pouring the nitric acid to the bottom of the aqueous glycerin, so that the liquids may mix gradually, the chief products are oxalic acid and glyceric acid,  $C^3H^4O^4$  (p. 876). When syrupy glycerin is added by drops to a mixture of equal volumes of strong nitric and sulphuric acids, cooled by a freezing mixture, a substitution-product, *nitroglycerin*,  $C^3H^5(NO^2)_3O^3$ , is formed.—9. Glycerin dissolved in a large quantity of water, and exposed to the air for several months in contact with well-washed *yeast*, gives off a few gas-bubbles, and is converted into propionic acid (Redtenbacher).—10. A moderately concentrated aqueous solution of glycerin (1 pt. glycerin to 10 pts. water) exposed to diffused daylight in an open flask in contact with certain *animal membranes* (the membrane of the testicle answers best), is converted, in an interval varying from one to twelve weeks, into glucose (Berthelot, p. 857). Glycerin gently heated with *hydrate of potassium* is converted into acetate and formate of potassium, with evolution of hydrogen:



11. With *cupric acetate* or *sulphate*, glycerin forms a deep blue liquid, which deposits

a small quantity of cuprous oxide when boiled. Potash throws down a precipitate which dissolves in excess of potash; formed deposits bluish flakes at 100° C.—12. From *gold* glycerin throws down a dark purple powder.—13. After several months in a bottle filled with *chlorine*, is converted into chloric acid, into a syrupy liquid, from which water separates a fusible substance, having an unpleasant ethereal odour at 14. Glycerin heated in sealed tubes with *bromine* and water yields glyceric acids, together with bromoform and carbonic anhydride; bromine is dropped into heated anhydrous glycerin, acrolein, an oil containing a small quantity of dibromhydrin, but principally bromoacetic acid, as, when treated with boiling water, it yields glycollic acid (Barth, Ann. Ch. Pharm. cxxiv. 341).—16. Without decomposition.—17. With *di-iodide of phosphorus* distillate of water and iodotriethylene (iodide of allyl), and a mixture of phosphorus, together with free iodine, undecomposed red phosphorus. The principal part of the action appears to be by the equation:



18. With *tribromide* and *pentabromide of phosphorus* glycerin (i. 667); several liquids which volatilise in vacuo at 200° also to be bromhydrins; a brominated compound, volatile acrolein; and dibromallylphosphine = P.H.(C<sup>3</sup>H<sup>5</sup>Br)<sub>2</sub> (Bert. Ch. Phys. [3] xlviii. 304).—19. Similarly with *trichloride of phosphorus*, glycerin yields the chlorhydrins (i. 893) though most of these compounds are more readily produced by the action of acid upon glycerin (Berthelot).—20. With *chloride of sulphur*, glycerin and another compound, which appears to be a glyceryl ether, the glycerin is heated for a considerable time with a little sulphur, trichlorhydrin is produced (Carius, Ann. Ch. Pharm. 21).

21. Glycerin heated with *acids* is, for the most part, transformed into glyceric ethers (p. 877), the proportions of the acid and the combination varying according to the proportions in the mixture, temperature and pressure to which the mixture is subjected; the action is continued: in most cases two or more compounds are formed. Thus, with *acetic acid* it forms the acetins (i. 25), (i. 1001), with *phosphoric anhydride* or *glacial phosphoric acid*, C<sup>3</sup>H<sup>5</sup>PO<sup>3</sup> (p. 891); with *strong sulphuric acid*, C<sup>3</sup>H<sup>5</sup>SO<sup>3</sup> (p. 892). With *cyanic acid* it forms allophanate of (i. 134). With *hydrobromic* and *hydrochloric acids* glycerin yields bromhydrins and chlorhydrins. When saturated with *hydroiodic acid* and heated for several hours, it yields the so-called iodhydrin, C<sup>3</sup>H<sup>5</sup>IO<sup>3</sup> (Berthelot of pyroglycide (p. 894): (C<sup>3</sup>H<sup>5</sup>)<sub>2</sub>H<sup>2</sup>O<sup>4</sup> + HI - H<sup>2</sup>O = C<sup>3</sup>H<sup>5</sup>IO<sup>3</sup>) a saturated solution of the same acid to 145° C. for five hours, and a liquid which yields, by distillation, iodide of glycerin, a compound is also formed abundantly when glycerin is distilled with iodine; however, the proportion of the latter is increased, the iodide appears, and is replaced by iodide of triethyl, C<sup>3</sup>H<sup>5</sup>I. The bromide of glycerin yields, when distilled with water, white needle-shaped crystals. If the same residue be exhausted with alcohol, then the water-bath to a syrup, and then mixed with potash, a white crystalline substance is obtained, which deposits white aromatic iodated crystals, not yet examined (Zeitsch. Ch. Pharm. 1861, pp. 362, 673.)

**Nitroglycerin.** C<sup>3</sup>H<sup>5</sup>N<sup>3</sup>O<sup>9</sup> = C<sup>3</sup>H<sup>5</sup>(NO<sup>3</sup>)<sub>3</sub>O<sup>3</sup>. Glonoin. (Compt. rend. xxiv. 247); further investigated by Railliet (222), and De Vrij (J. Pharm. [3] xxviii. 38). A compound of a mixture of strong nitric and sulphuric acids on glycerin.

**Preparation.**—1. A hundred grammes of syrupy glycerin are gradually added to 200 c. c. of nitric acid of specific gravity 1.52, the mixture being continually stirred, the temperature being kept below 10° C. before each fresh addition, and never to rise above 15° C. when the mixture having been thus obtained, 200 c. c. of strong sulphuric acid, the mixture being still kept below 10°. The oily mixture which then floats on the surface is separated by a tap-funnel (which yields 20 grms. more of nitroglycerin on being diluted

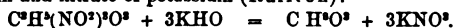


in the smallest possible quantity of ether: the solution is repeatedly shaken with water till the water no longer reddens litmus; the ether evaporated; and the remaining nitroglycerin heated over the water-bath till its weight remains constant. The product amounts to 184 grms. of pure nitroglycerin (De Vrij). According to Railton, nitroglycerin is decomposed by evaporation, even in vacuo over sulphuric acid, at ordinary temperatures.

2. Half an ounce of dehydrated glycerin is poured, with constant stirring, into a mixture of 2 oz. of oil of vitriol and 1 oz. fuming nitric acid of specific gravity 1.52, the temperature of the mixture being kept below 25° C. by external cooling with ice; and, as soon as oily drops begin to form on the surface, the mixture is poured, with constant stirring, into 50 ounces of cold water. Nitroglycerin then separates, and may be purified by washing and drying, in small portions, in a vapour-bath. (Liebe, Arch. Pharm. ciii. 158; civ. 282—See also Sobrero, Rép. Chim. app. ii. 400.)

*Properties.*—Nitroglycerin is a light yellow oily liquid, of specific gravity 1.595 to 1.600, at 15° C. (De Vrij); inodorous, but has a sweet pungent aromatic taste, and when placed upon the tongue, even in small quantity, produces headache, which lasts for several hours (Sobrero). Slightly soluble in water, more soluble in alcohol and in ether.

Nitroglycerin, when left to itself, frequently undergoes spontaneous decomposition, but, when well purified, it may be kept for a long time without alteration. De la Rue and Müller (Ann. Ch. Pharm. cix. 122) found glyceric acid among the products of decomposition of nitroglycerin, which had been left to itself in an apartment the temperature of which rose sometimes to about 30° C. Oxalic acid was likewise formed, together with an acid the barium-salt of which was not crystallisable. At 160° C. it decomposes, with evolution of red vapours, and at higher temperatures sometimes explodes with sufficient violence to shatter the containing vessel; sometimes takes fire without explosion. It detonates when struck. Mixed with fuming *hydriodic acid*, it decomposes below 100° C., yielding glycerin and pure nitric oxide (Mills). Its ethereal solution is decomposed by *sulphydic acid*, with copious precipitation of sulphur (De Vrij). Nitroglycerin, heated with aqueous *potash*, is decomposed, with formation of glycerin and nitrate of potassium (Railton):



According to Gladstone, nitroglycerin exhibits different properties according to the manner in which it is prepared. Ordinary hydrated glycerin added to a mixture of 3 pts. sulphuric and 1 pt. fuming nitric acid, is converted into a liquid which detonates violently under the hammer; but anhydrous glycerin treated in like manner yields a non-explosive body which burns without noise. Both kinds of nitroglycerin, when exposed to a mixture of solid carbonic acid and alcohol, become gummy, and assume the appearance of fatty acids; and both decompose spontaneously, with evolution of red vapours. A sample of nitroglycerin which decomposed in this manner on exposure to summer sunshine, yielded crystals of oxalic acid, together with two liquids, the upper of which contained nitric acid, ammonia, oxalic acid, hydrocyanic acid, and other compounds not examined (Reports of the British Association, 1856; Jahresb. d. Chem. 1857, 479.) Mills found that nitroglycerin kept for a fortnight no longer exploded when struck, but showed no signs of decomposition or chemical alteration. (Communication from G. C. Foster.)

**GLYCEROCITRIC ACID.** *Citroglyceric acid.*—Obtained by heating a mixture of glycerin and citric acid not strongly enough to produce the citric ethers of glycerin described at p. 1001, vol. i. (Van Bemmelen, Scheik. Onderzoek. ii. 1; Jahresb. 1859, p. 434.) Lourenço has obtained a glycerocitric acid containing  $\text{C}^6\text{H}^{14}\text{O}^8$  (p. 894).

**GLYCERO-OXALIC ACID.** *Oxaloglyceric acid.*—This acid is produced when oxalic acid is heated with glycerin, before the temperature has risen high enough to induce the resolution of the oxalic acid into formic acid and carbonic oxide (p. 686). Its calcium-salt is soluble in water, and the solution is not precipitated by alcohol, but deposits oxalate of calcium when heated after addition of ammonia. (Van Bemmelen, loc. cit.)

**GLYCEROPHOSPHORIC ACID.** *Phosphoglyceric acid.*  $\text{C}^3\text{H}^5\text{PO}^4 = (\text{PO})^{\text{III}} \cdot \text{C}^3\text{H}^5 \cdot \text{O}^8$ . (Pelouze, Compt. rend. xii. 718.—Gobley, J. Pharm. [3], ix. 161; xi. 409; xii. 5.—Gm. ix. 492; Gerh. i. 770.)—This acid exists in the yolk of eggs and in the brain (Gobley), and is produced by the action of phosphoric acid or phosphoric anhydride on glycerin (Pelouze). To obtain it in this way, glycerin is mixed with excess of phosphoric anhydride, or glacial phosphoric acid; the mixture is dissolved in water, and neutralised, first with carbonate of barium, then with baryta-water; the solution is filtered from phosphate of barium, and treated with a quantity of sulphuric acid just sufficient to precipitate the baryta; and the filtrate is evaporated in vacuo.



To obtain it from the yolk of eggs, that substance is freed from water by heat, then exhausted with boiling alcohol or ether, the residue, consisting of egg-oil and a viscid substance, collodion, is drained in the hot air chamber till the greater part of the residual viscid matter is pressed between folds of paper, and is thereby extracted. The soft, orange-yellow, translucent mass is then heated with dilute potash in the water-bath for 24 hours, supersaturated with acetic acid, and filtered from oleic matter, precipitated with neutral acetate of lead; the precipitate is washed, suspended in water, and decomposed by sulphhydric acid, treated by gentle evaporation, and freed from a small quantity of silver by agitation with a small quantity of oxide of silver and filtrated by sulphhydric acid; the filtered liquid freed from a small quantity of calcium by saturation with lime-water; the liquid separated as phosphate of calcium, and the solution of glycerophosphate of crystallising point. The crystals are purified by again dissolving, and recrystallising; the lime precipitated from their acervant quantity of oxalic acid; and the filtrate evaporated to dryness.

Glycerophosphoric acid is also produced by the action of phosphoretted fat contained in the brain. (Strecker, *Compt. Rend.* 1845, 1846.)

Glycerophosphoric acid is an uncrystallisable liquid. It is evaporated to a certain point, but beyond that it decomposes into glycerin. When concentrated in vacuo, it thickens and has a very acid taste, is very soluble in water and in alcohol, and strongly acid cinder.

The glycerophosphates are for the most part sparingly soluble in alcohol.

The *barium-salt*,  $C^3H^3Ba^2PO^6$  (at  $150^\circ C.$ ), is very soluble in water from the solution by alcohol.

The *calcium-salt*,  $C^3H^3Ca^2PO^6$  (at  $120^\circ C.$ ), forms snow-white crystals, but having a rather sharp taste. It sustains a high temperature, but blackens at a somewhat stronger heat. When dissolved in water, it is resolved into phosphate of calcium and glycerin abundantly in cold than in boiling water, so that it separates on cooling. From the aqueous solution it is precipitated by the cold solution on boiling.

The *lead-salt*,  $C^3H^3Pb^2PO^6$ , is insoluble in water.

#### GLYCEROSULPHURIC ACID. *Sulphoglyceric Acid*

—(Pelouze, *Ann. Ch. Phys.* lxxiii. 21; *Gm. ix.* 494; Gerhardt, *action of strong sulphuric acid upon glycerin.* 1 pt. of glyceric acid; the mass, when cold, is dissolved in water; lime, filtered, and evaporated to a syrup; the crystals of the syrup on cooling are collected and dissolved in water; the lime is removed by the proper quantity of oxalic acid; and the liquid is evaporated to dryness.

By this process, *aqueous glycerosulphuric acid* is obtained, an inodorous, strongly acid liquid, which is so unstable that it decomposes into acid and glycerin when evaporated in vacuo at a few degrees, still retains a considerable quantity of water.

The aqueous acid decomposes carbonates. The glycerates are very soluble in water. The potassium, sodium, and calcium salts, sulphurous anhydride, acrylic acid, acrolein, and decomposition. (Redtenbacher, *Ann. Ch. Pharm.* xlvii.)

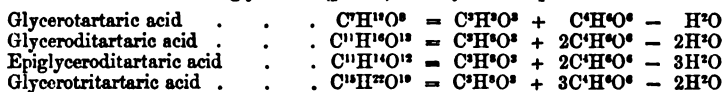
The *barium-salt* is decomposed, when its aqueous solution is below  $100^\circ C.$ , into sulphate of barium, which is precipitated by glycerin.

The *calcium-salt*,  $C^3H^3CaSO^6$ , forms colourless needles. It begins to decompose between  $140^\circ$  and  $150^\circ C.$ , emitting a distilled tallow, and leaves, first a carbonaceous residue, then phosphate of calcium. The aqueous solution is not decomposed at ordinary temperatures, but after boiling for a short time with lime-water. The crystallised salt dissolves in less than 1 pt. of water or ether.

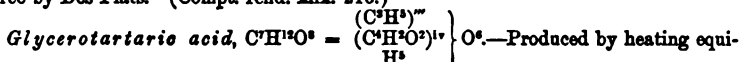
The *lead* and *silver* salts are soluble in water.

The *sulpholeous acid* (*schwefelölige Säure*), which is obtained by olive-oil with sulphuric acid, and the *sulphadipic acid* of Hog's lard by Chevreul, were perhaps identical with glycerosulphuric acid.

**GLYCEROTARTARIC ACIDS.** By heating tartaric acid and glycerin in various proportions and to various temperatures, four acids are obtained, the formation of which is attended with elimination of quantities of water less than would be required for the formation of normal glycerides (p. 877). They are composed as follows:



The first of these acids was discovered by Berzelius (*Traité de Chimie*); the other three by Des Plats. (Compt. rend. xlix. 216.)



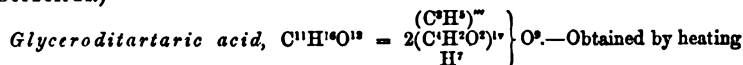
valent quantities of glycerin and coarsely pounded tartaric acid (or effloresced paratartaric acid), to about 150° C. (Berzelius); by heating equal weights of glycerin and tartaric acid to 100° C. for forty hours (Des Plats). The mixture on cooling is transparent, and solidifies to a soft ropy mass. It is inodorous, has a faint but purely acid taste, absorbs moisture from the air, and changes to a thick syrup. It is insoluble in pure ether, but dissolves easily in ether-alcohol. In the syrupy state, it may be preserved unaltered. Neither carbonate nor acetate of potassium, added to it in small quantity, produces any precipitate of acid tartrate of potassium.

The syrupy acid, mixed with a large quantity of water, is partly resolved into glycerin and tartaric acid; the decomposition is accelerated by warming the liquid, but on evaporating the mixture and again heating it to 150° C., the glycerotartaric acid is reproduced.

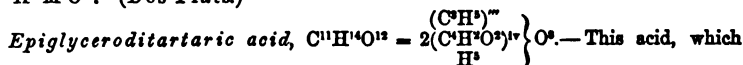
Glycerotartaric acid expels carbonic acid from alkaline and earthy carbonates, forming soluble salts which have a gummy aspect. The glycerotartarates are insoluble in alcohol, which precipitates them from aqueous solution. They are tasteless. The neutral salts, dissolved in a large quantity of water and evaporated, decompose, yielding glycerin and tartaric acid (Berzelius). The decomposition is accelerated by addition of baryta- or lime-water. (Des Plats.)

The barium-salt contains  $\text{C}^1\text{H}^1\text{BaO}^8$ .

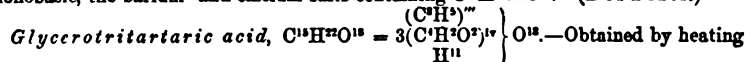
*Glycerotartrate of calcium*,  $\text{C}^1\text{H}^1\text{CaO}^8 + \frac{2}{3} \text{aq.}$ , is prepared by saturating aqueous glycerotartaric acid with carbonate of calcium, evaporating, filtering to remove a quantity of tartrate of calcium which separates in confused crystals, and adding alcohol to the concentrated solution. It then separates in the form of a thick pulp, which sticks to the sides of the vessel when the liquid is agitated; the portion which remains suspended in the alcohol takes several days to settle down. On dissolving the precipitated salt in a small quantity of water, and filtering to separate any small portion of tartrate that may be present, a colourless solution is obtained, which may be evaporated without decomposition at a gentle heat. The residue forms a colourless mass, having the lustre and aspect of glass, and splitting when dried. The salt is not deliquescent; it cannot be deprived of its crystallisation-water without decomposition. (Berzelius.)



equal weights of glycerin and tartaric acid with a certain quantity of water to 100° C. for fifty hours. It is dibasic, its barium- and calcium-salts having the composition  $\text{C}^{11}\text{H}^{14}\text{M}^2\text{O}^{12}$ . (Des Plats.)



is related to the preceding in the same manner as epidichlorhydrin to dichlorhydrin, is obtained by heating equal weights of glycerin and tartaric acid to 140° C. It is monobasic, the barium- and calcium-salts containing  $\text{C}^{11}\text{H}^{14}\text{MO}^{12}$ . (Des Plats.)



1 pt. glycerin with 20 pts. tartaric acid to 140° C., or 1 pt. glyceroditartaric acid with 15 pts. tartaric acid for 30 hours. It is tetrabasic, the barium and calcium-salts containing  $\text{C}^{18}\text{H}^{22}\text{M}^4\text{O}^{18}$ . (Des Plats.)

**GLYCERYL.**  $\text{C}^3\text{H}^3$ . The triatomic radicle of glycerin and the glycerides.

**GLYCERYL, BROMHYDRATES and BROMIDE OF.** See BROMHYDRINS (i. 667).





*Diglycide, Pyroglycide, or Metaglycerin*,  $C^3H^5O^4$ , which has the composition of pyroglycerin minus  $H^2O$ , is obtained from that portion of the distillate *A* (p. 894) which passes over under the ordinary atmospheric pressure between  $170^\circ$  and  $270^\circ$  C. (and consists of dichlorhydrin, together with the chlorhydric ethers of the polyglyceric alcohols) by cautiously decomposing the portion boiling between  $230^\circ$  and  $270^\circ$  with ignited potash, distilling the liquid decanted from the chloride of potassium which separates, and collecting the portion which goes over between  $245^\circ$  and  $255^\circ$ . It is a colourless oil, soluble in water and in alcohol, insoluble in ether.

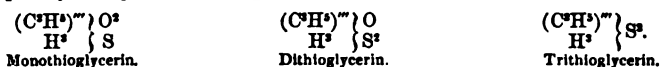
Polyglyceric compounds may also be obtained by distilling glycerin under the ordinary atmospheric pressure, and treating the portion which goes over between  $130^\circ$  and  $260^\circ$  C. with ether. The undissolved portion boils at a temperature above  $300^\circ$  under a pressure of 10 mm., and yields polyglyceric compounds. The glycerin is, perhaps, first converted into glycide, by loss of water ( $C^3H^5O^3 - H^2O = C^3H^4O^3$ ), and the glycide then unites with 1, 2, or 3 at. glycerin, forming the polyglyceric compounds. (Lourengo.)

**GLYCERYL, IODHYDRATES OF.** See IODHYDRINS.

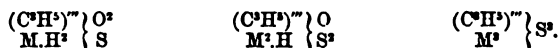
**GLYCERYL, OXIDE OF.**  $C^3H^4O^3 = \frac{C^3H^4}{C^3H^3} \left\{ O^2 \right\}$ .—Obtained by the action of potash on iodhydrin. It is a liquid soluble in ether and volatile without decomposition. (Berthelot.)

**GLYCERYL, OXYGEN-SALTS OF.** See ACETINS, BENZOINS, BUTYRINS, &c.

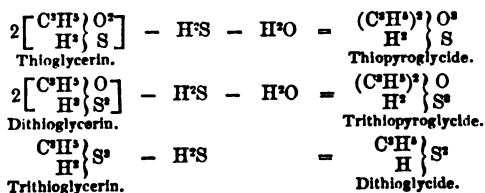
**GLYCERYL, SULPHYDRATES OF.** *Thioglycerins*. (Carius, Ann. Ch. Pharm. cxxii. 72; cxxiv. 222.)—The oxygen of glycerin may be wholly or partly replaced by sulphur, yielding the three compounds:



These compounds are produced by the action of alcoholic sulphhydrate of potassium on mono-, di- and trichlorhydrin. They are syrupy liquids of unpleasant ethereal odour, soluble in alcohol, very sparingly soluble in water, insoluble in ether. They react with metallic oxides and salts like sulphhydrate of ethyl (mercaptan), forming compounds in which the typic hydrogen is more or less replaced by a metal, in proportion to the number of sulphur-atoms in the thioglycerin. The general formulæ of the metallic derivatives of the three thioglycerins are therefore:



The thioglycerins are decomposed by heat, trithioglycerin giving off sulphydric acid, and leaving dithioglycide, while the other two compounds give both sulphydric acid and water, and yield sulphuretted compounds analogous to pyroglycide; thus:

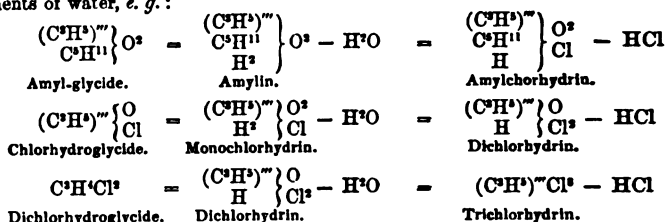


The thioglycerins are oxidised by nitric acid, forming glycerosulphurous ethers, monothioglycerin yielding *glycerin-monosulphurous acid*, which is monobasic, and dithioglycerin yielding *pyroglyci-trisulphurous acid*, a dibasic acid related in composition to trithiopyroglycide. The salts of these acids are represented by the formulæ:



**GLYCIDE.**  $C^3H^4O^3 = \frac{C^3H^4}{H} \left\{ O^2 \right\}$ .—The hypothetical alcohol corresponding to the glycidic ethers. It differs from glycerin, in the same manner as oxide of ethylene,  $C^2H^4O$ , differs from glycol,  $C^2H^6O^2$ , viz. by 1 at. water.

**GLYCIDIC ETHERS.** (Reboul, Ann. Ch. Phys. [3] ix. 6; Jahresb. 186 p. 454.)—A class of diatomic ethers, closely related to the glycerides, and produced from them by the action of alkalis. They differ from some of the triatomic glycerides by the elements of hydrochloric, hydrobromic, or hydriodic acid; from others by the elements of water, *e. g.*:

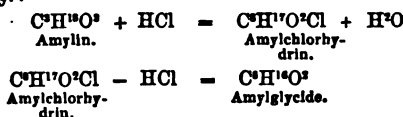


There are two series of glycidic ethers, which may be derived from the hypothetical diatomic alcohol glycide,  $\text{C}^{\text{H}^3}\text{O}^2$ , according to the general formulæ:



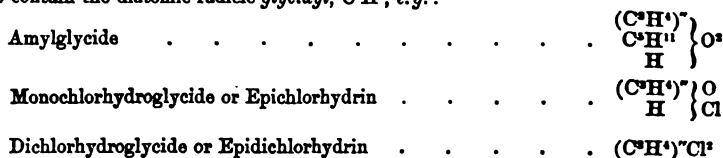
the symbols A, A', denoting monatomic acids or alcohols. The first series includes Berthelot's epichlorhydrin, epibromhydrin, &c., which differ from monochlorhydrin, &c. by 1 at.  $\text{H}^2\text{O}$ ; the second series includes epidichlorhydrin, &c., which differ in like manner from dichlorhydrin, &c.

The glycidic ethers are not produced from the corresponding triatomic glycerides by direct abstraction of water; but they are obtained directly from the triatomic glycerides containing chlorine, bromine, &c., by the action of alkalis, which abstract hydrochloric, hydrobromic acid, &c. To convert a glycerin-ether not containing chlorine, bromine, or iodine, into a glycidic ether, it must first be converted into a chlorhydrin by the action of hydrochloric acid, and this compound then treated with an alkali to abstract hydrochloric acid, *e. g.*:



Conversely, the glycidic ethers containing chlorine, bromine, &c. are converted by the action of oxygen-acids, water, and alcohols, into triatomic glycerin-ethers (p. 862).

Reboul, by whom the glycidic ethers have been particularly studied, supposes them to contain the diatomic radicle *glycidyl*,  $\text{C}^{\text{H}^3}$ , *e. g.*:



But the relations of the first series of these compounds ( $\text{C}^{\text{H}^3}\text{O}^2 + \text{A} - \text{H}^2\text{O}$ ) to the glycerides may be more simply represented, as first suggested by Erlenmeyer (Zeitschr. Ch. Pharm. 1860, p. 737), by supposing them to contain the same radicle as the glycerides, viz.  $\text{C}^{\text{H}^3}$ , that is to say, by regarding them as the ethers of the diatomic alcohol,  $\left. \begin{array}{c} (\text{C}^{\text{H}^3})^{\text{m}} \\ \text{H} \end{array} \right\} \text{O}^2$ , related to glycerin in the same manner as monometaphosphoric acid,  $\left( \text{PO} \right)^{\text{m}} \left\{ \text{O}^2 \right.$ , to orthophosphoric acid,  $\left( \text{PO} \right)^{\text{m}} \left\{ \text{O}^2 \right.$ ; *e. g.* *amylglycide*,  $\left. \begin{array}{c} (\text{C}^{\text{H}^3})^{\text{m}} \\ \text{C}^{\text{H}^1} \end{array} \right\} \text{O}^2$  *epichlorhydrin*,  $\left. \begin{array}{c} (\text{C}^{\text{H}^3})^{\text{m}} \\ \text{Cl} \end{array} \right\}$  &c.

The glycidic ethers of the second series ( $\text{C}^{\text{H}^3}\text{O}^2 + \text{A} + \text{A}' - 2\text{H}^2\text{O}$ ), such as epidichlorhydrin, cannot be represented exactly in the same manner, because they contain only 4 at. hydrogen; they may, however, be regarded as chlorides, bromides &c. containing monatomic radicles formed from  $\text{C}^{\text{H}^3}$  by the substitution of Cl, Br &c. for 1 at. H.—epidichlorhydrin,  $\text{C}^{\text{H}^3}\text{Cl}^2$ , for example, then becoming *chloride of chlor allyl*,  $(\text{C}^{\text{H}^3}\text{Cl})\text{Cl}$ .

These ethers are not so closely related to the glycerides as those of the first series. They do not yield glycerin when boiled with alkalis; neither are they converted into

glycerides by the action of water or of alcohols, or generally speaking of acids, although Reboul states that epidichlorhydrin is very slowly converted into trichlorhydrin by boiling with hydrochloric acid. It is, however, most convenient to describe them in connection with the glycidic ethers of the first series, to which they are certainly related by their mode of formation.

The polyglyceric compounds and the glycidic ethers of the first series are related to glycerin in the same manner as metaphosphoric acid and some of its modifications to orthophosphoric acid: this will be seen from the following table:

Types . .	2H <sup>2</sup> O.	3H <sup>2</sup> O.	4H <sup>2</sup> O.	5H <sup>2</sup> O.	6H <sup>2</sup> O.	7H <sup>2</sup> O.	9H <sup>2</sup> O.
Glycidic Series .	$\left( \begin{smallmatrix} \text{C}^2\text{H}^4 \\ \text{H} \end{smallmatrix} \right)^m \text{O}^2$	$\left( \begin{smallmatrix} \text{C}^2\text{H}^4 \\ \text{H}^2 \end{smallmatrix} \right)^m \text{O}^3$	$\left( \begin{smallmatrix} \text{C}^2\text{H}^4 \\ \text{C}^2\text{H}^4 \\ \text{H}^2 \end{smallmatrix} \right) \text{O}^4$	$\left( \begin{smallmatrix} \text{C}^2\text{H}^4 \\ \text{C}^2\text{H}^4 \\ \text{H}^2 \end{smallmatrix} \right) \text{O}^5$	$\left( \begin{smallmatrix} \text{C}^2\text{H}^4 \\ \text{C}^2\text{H}^4 \\ \text{C}^2\text{H}^4 \\ \text{H}^2 \end{smallmatrix} \right) \text{O}^6$	$\left( \begin{smallmatrix} \text{C}^2\text{H}^4 \\ \text{C}^2\text{H}^4 \\ \text{C}^2\text{H}^4 \\ \text{H}^2 \end{smallmatrix} \right) \text{O}^7$	$\left( \begin{smallmatrix} \text{C}^2\text{H}^4 \\ \text{C}^2\text{H}^4 \end{smallmatrix} \right) \text{O}^9$
	Glycide.	Glycerin.	Diglycide.	Diglycerin.	Triglycide.	Triglycerin.	Glyceric anhydride.
Phosphoric Series .	$\left( \begin{smallmatrix} \text{PO} \\ \text{H} \end{smallmatrix} \right)^m \text{O}^2$	$\left( \begin{smallmatrix} \text{PO} \\ \text{H}^2 \end{smallmatrix} \right)^m \text{O}^3$	$\left( \begin{smallmatrix} \text{PO} \\ \text{PO} \\ \text{Na}^2 \end{smallmatrix} \right) \text{O}^4$	$\left( \begin{smallmatrix} \text{PO} \\ \text{PO} \\ \text{H}^2 \end{smallmatrix} \right) \text{O}^5$	$\left( \begin{smallmatrix} \text{PO} \\ \text{PO} \\ \text{PO} \\ \text{Na}^2 \end{smallmatrix} \right) \text{O}^6$		$\left( \begin{smallmatrix} \text{PO} \\ \text{PO} \end{smallmatrix} \right) \text{O}^9$
	Metaphosphoric acid.	Orthophosphoric acid.	Maddrell's metaphosphate of sodium.	Pyrophosphoric acid	Fleitmann and Henneberg's metaphosphate of sodium.		Phosphoric anhydride.

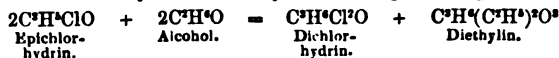
The polyglycerides constitute the intermediate links between glycide and the true glyceric ether or glyceride anhydride. (*Kekulé's Lehrbuch*, ii. 117.)

The greater number of the following compounds have been prepared and partially described by Berthelot (See BROMHYDRINS and CHLORHYDRINS); but the experiments of Reboul have rendered our knowledge of them much more exact.

#### A. Glycidic ethers containing 1 at. acid- or alcohol-radicle.

**Amylglycide.**  $\text{C}^2\text{H}^4\text{O}^2 = \left( \begin{smallmatrix} \text{C}^2\text{H}^4 \\ \text{C}^2\text{H}^4 \end{smallmatrix} \right)^m \text{O}^2$ .—Produced by the action of potash on amylchlorhydrin (p. 884). When a mixture of equal volumes of epichlorhydrin and amyl alcohol is heated to 220° C. for ten or twelve hours in a sealed tube; the resulting yellowish oily liquid distilled; the portion which goes over between 225° and 260°, and contains amylchlorhydrin, shaken up with excess of strong boiling potash-ley; the oil which separates from the resulting solution of chloride of potassium on addition of water distilled; and the portion which passes over between 180° and 220° C. several times rectified,—amyglycide is obtained as a mobile liquid of specific gravity 0.90 at 20° C., and having an odour of ripe quinces. It is insoluble in water, boils at 188°, is inflammable, and burns with a bright flame. By agitation with fuming hydrochloric acid, it is converted into amylchlorhydrin,  $\text{C}^2\text{H}^4(\text{C}^2\text{H}^4)\text{O}^2$ , and by hydrobromic and hydriodic acids, into the corresponding brom- and iod-hydrins. Heated with water in sealed tubes, it takes up H<sup>2</sup>O, and is converted into amylin,  $\text{C}^2\text{H}^4(\text{C}^2\text{H}^4)\text{O}^2$ .

**Ethylglycide.**  $\text{C}^2\text{H}^4\text{O}^2 = \left( \begin{smallmatrix} \text{C}^2\text{H}^4 \\ \text{C}^2\text{H}^4 \end{smallmatrix} \right)^m \text{O}^2$ .—Produced by the action of potash on ethylchlorhydrin. The formation of this latter compound, by heating epichlorhydrin with ethylic alcohol in sealed tubes to 180° C., is attended with the production of considerable quantities of dichlorhydrin and diethylin, according to the equation:



The greater part of the resulting liquid distils between 188° and 189° C.; and the distillate, treated with potash, yields an ethereal oil which distils for the most part between 126° and 130°, and consists of ethylglycide mixed with a considerable quantity of epichlorhydrin (produced by the action of the alkali on the dichlorhydrin). The ethylglycide may be freed from the greater part of the epichlorhydrin by treatment with alcoholic potash. It is a mobile liquid, having a faint but agreeable ethereal odour, boiling between 128° and 129° C., and of nearly the same density as water. It dissolves in 4 or 5 times its volume of cold water, somewhat more freely in



hot water, and is separated from the solution by chloride of calcium. Its reactions are similar to those of amylglycide.

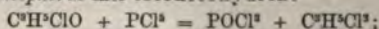
**Monobromhydroglycide.** *Epibromhydrin*.  $(C^2H^3)^m \begin{Bmatrix} Br \\ O \end{Bmatrix}$ . — Produced by the action of alkalis on dibromhydrin; also, together with other products, by the action of pentachloride of phosphorus on glycerin (p. 890). It boils at  $138^\circ$ — $140^\circ$  C., united with fuming hydrochloric acid, forming bromochlorhydrin,  $C^2H^3BrClO$ , and with hydriodic acid, forming iodobromhydrin. (See IODHYDRINS.)

**Monochlorhydroglycide.** *Epichlorhydrin*.  $(C^2H^3)^m \begin{Bmatrix} Cl \\ O \end{Bmatrix}$ . — Produced by the action of alkalis on dichlorhydrin. To prepare the latter, a mixture of 5 vols. glycerin (the commercial product dehydrated by heating it to about  $170^\circ$  C. may be used) and 4 vols. glacial acetic acid is saturated at  $100^\circ$  C. with hydrochloric acid gas, and then distilled; whereby a distillate is obtained between  $180^\circ$  and  $220^\circ$  C. consisting of dichlorhydrin, mixed with a large quantity of acetodichlorhydrin and a small quantity of acetochlorhydrin. This distillate may be used immediately for the preparation of epichlorhydrin (the acetodichlorhydrin being converted by the potash into dichlorhydrin, with formation of acetate of potassium). For this purpose a lukewarm solution of 350 grms. caustic potash in the smallest possible quantity of water, is added by small portions to 500 grms. of the distillate just mentioned, the liquid being well shaken and left to cool after each addition; the whole is then left to itself for an hour or two; the oily layer which floats on the surface is removed and distilled; the portion which goes over below  $165^\circ$  C. is collected apart; and this by repeated fractional rectification, yields pure epichlorhydrin.

Epichlorhydrin is a mobile liquid, of specific gravity 1.194 at  $11^\circ$  C.; it boils at  $118^\circ$  or  $119^\circ$ ; smells like chloroform; has a sweet taste, with burning aftertaste; burns with a bright, smoky, green-edged flame. It is nearly insoluble in water, but takes up a small quantity of it, and retains it obstinately; soluble in all proportions in alcohol and ether. Its vapour-density is by experiment = 3.21; by calculation (2 vols.) = 3.19.

Strong sulphuric acid acts violently on epichlorhydrin; if it is added by drops, and the liquid kept cool, no hydrochloric acid is evolved, but the liquid becomes viscid, and a so-called conjugated sulphuric acid appears to be formed.

Chloride of zinc likewise acts violently on epichlorhydrin, hydrochloric acid being evolved and the mass blackening if not sufficiently cooled, whereas if the temperature is prevented from rising, the two substances simply unite. Epichlorhydrin is converted by pentachloride of phosphorus into trichlorhydrin:

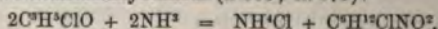


and by pentabromide of phosphorus into chlorodibromhydrin,  $C^2H^3Br^2Cl$  (i. 894) a liquid of specific gravity 2.085 at  $9^\circ$  C., and boiling at  $202^\circ$ — $203^\circ$ .

Epichlorhydrin heated with alcoholic ammonia to  $100^\circ$  C. in a closed vessel forms chloride of ammonium, and a white gummy mass, consisting of diglyceryl

dihydrochloramine, or hemichlorhydrinamide,  $C^6H^{12}ClNO^2 = \begin{matrix} C^2H^3 \\ N \\ O^2 \end{matrix} \begin{matrix} H \\ Cl \end{matrix}$ , and

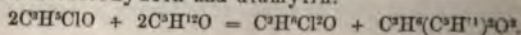
logous to Berthelot's hemibromhydrinamide (i. 668; ii. 875):



With cold aqueous ammonia, epichlorhydrin thickens and gradually dissolves; and the liquid, after neutralisation with hydrochloric acid, contains chloride of ammonium, and an uncrystallisable salt, from whose highly concentrated solution caustic potash throws down a reddish gummy base, which redissolves on the addition of a small quantity of water.

Epichlorhydrin unites directly with hydrochloric acid, forming dichlorhydrin,  $C^2H^3Cl^2O$  (boiling at  $180^\circ$  C.); with hydrobromic acid, forming bromochlorhydrin,  $C^2H^3BrClO$  (a colourless oily liquid of specific gravity 1.740 at  $12^\circ$  C., boiling at  $197^\circ$  having a faint odour like that of dichlorhydrin, sparingly soluble in water); and with hydriodic acid, forming iodochlorhydrin,  $C^2H^3IClO$  (see IODHYDRINS). The combination is in all cases attended with evolution of heat, which is considerable when epichlorhydrin is agitated with fuming hydrochloric acid; stronger with fuming hydrobromic acid; and especially violent with fuming hydriodic acid, each drop of the acid producing a hissing noise.

Epichlorhydrin heated with amylic alcohol in sealed tubes, unites with it, forming amyl-chlorhydrin; but at the same a secondary reaction takes place, resulting in the formation of dichlorhydrin and diamylin:



With *ethyl alcohol* a similar reaction takes place, but the secondary products bear a larger proportion to the ethylchlorhydrin produced by direct combination (p. 897).

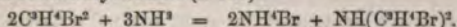
**Mono-iodhydroglycide.** *Epi-iodhydrin*,  $C^3H^3IO$ .—This compound cannot be prepared in the same manner as the two preceding, inasmuch as di-iodhydrin has not been obtained, not being produced from glycerin by the action either of hydriodic acid or of iodide of phosphorus. *Epi-iodhydrin* may, however, be prepared by heating epichlorhydrin with iodide of potassium to  $100^\circ$  in a sealed tube, care being taken to purify the materials from water as much as possible, since its presence would give rise to the formation of iodhydrin,  $C^3H^3IO^2$ . On treating the product of the reaction with a small quantity of water, to dissolve chloride of potassium and the excess of iodide, there remains a heavier liquid, from which, by distillation and repeated rectification of the portion which distils between  $160^\circ$  and  $180^\circ C.$ , pure *epi-iodhydrin* is obtained.

*Epi-iodhydrin* is a mobile ethereal liquid, having a somewhat alliaceous odour; specific gravity 2.03 at  $13^\circ C.$ ; insoluble in water; soluble in all proportions in alcohol and ether. With *hydrochloric acid* it forms iodochlorhydrin,  $C^3H^3IClO$ , identical with the compound formed by the combination of HI and  $C^3H^3ClO$ ; with *hydriodic acid*, it yields a viscid heavy liquid, strongly coloured by iodine, and probably containing di-iodhydrin,  $C^3H^3IO^2$ .

#### B. Glycidic ethers containing 2 at. Bromine, Chlorine, &c.

These compounds are produced by the action of alkalis on the triatomic glycerides containing 3 at. Br, Cl, &c.

**Dibromhydroglycide.** *Epidibromhydrin*,  $(C^3H^3)^2Br^2$  or  $(C^3H^3Br)^2$ .—Obtained by treating tribromhydrin,  $C^3H^3Br^3$ , with solid hydrate of potassium (a small quantity of acrolein being formed at the same time); distilling the heavy oil which passes over; and rectifying the portion which distils below  $156^\circ C.$  It is a liquid, insoluble in water, of specific gravity 2.06 at  $11^\circ C.$ , having a distinctly alliaceous odour, and boiling at  $161^\circ$ — $152^\circ C.$  It is decomposed by *alcoholic ammonia*, slowly in the cold, completely by heating for several hours to  $100^\circ C.$ , yielding bromide of ammonium and dibromallylamine (i. 146):



The formation of this base tends to support the supposition that the compound  $C^3H^3Br^2$  contains the monatomic radicle  $C^3H^3Br$  (p. 896).

*Epidibromhydrin* unites directly with 2 at. *bromine*, forming the compound  $C^3H^3Br^4 = (C^3H^3Br)^2Br^2$ , a liquid of specific gravity 2.64, and boiling, with slight evolution of hydrobromic acid, at  $250^\circ$ — $252^\circ C.$

**Dichlorhydroglycide.** *Epidichlorhydrin*,  $(C^3H^3)^2Cl^2$  or  $(C^3H^3Cl)^2$ .—Metameric with dichlorotriethylene. When trichlorhydrin is gently heated with lumps of solid potash, chloride of potassium is formed, with rise of temperature and violent action, and a distillate is obtained, consisting of water, with a lower layer of liquid, which, when freed from a small quantity of epichlorhydrin by agitation with sulphuric acid diluted with half its bulk of water, and distilled, yields *epidichlorhydrin*, as a liquid boiling with partial decomposition between  $101^\circ$  and  $102^\circ C.$ , of specific gravity 1.21 at  $20^\circ$ , having a pungent, ethereal, somewhat alliaceous odour, insoluble in water, soluble in all proportions in alcohol and ether. It unites slowly at  $100^\circ C.$  with *hydrochloric*, *hydrobromic*, and *hydriodic acids*, forming triatomic glycerides; with water and alcohols it does not unite, even at  $100^\circ$ . It unites directly with 2 at. *bromine*, forming the compound  $C^3H^3Cl^2Br^2 = (C^3H^3Cl)^2Br^2$ , a liquid insoluble in water, of specific gravity 2.10 at  $13^\circ C.$ , boiling at  $220^\circ$ — $221^\circ$ .

**Chlorobromhydroglycide.** *Epichlorobromhydrin*,  $(C^3H^3)^2ClBr$ , or  $(C^3H^3Cl)Br$ , or  $(C^3H^3Br)Cl$ .—Produced by heating chlorodibromhydrin (i. 874; ii. 898) with solid potash, and purified like the preceding compound. Colourless liquid, turning yellow when exposed to light; smells like *epidichlorhydrin*; boils at  $126^\circ$ — $127^\circ C.$  Specific gravity 1.69 at  $14^\circ C.$  It is not perceptibly decomposed by heating with water to  $100^\circ C.$  for two days. Not attacked by sodium in the cold, but slowly when heated, with formation of bromide of sodium. It unites directly with 2 at. *bromine*, forming the compound  $C^3H^3ClBr^3 = (C^3H^3Cl)Br^3$ , a liquid of specific gravity 2.39 at  $14^\circ C.$ , and boiling, with slight evolution of hydrobromic acid, at  $238^\circ$ .

**GLYCIDYL.**  $C^3H^3$ .—The diatomic radicle which may be supposed to exist in the glycidic ethers (p. 896).

**GLYCOCHOLIC ACID.**  $C^3H^3NO^4$ .—This acid, discovered by L. Gmelin (*Handbuch*, 3<sup>re</sup> Aufl. ii. 833), constitutes, in the form of a sodium-salt, the essential part of ox-bile, in which it is mixed with small quantities of taurocholic acid, mucus, cholesterin, cholochrome, &c. (i. 585). Its composition and metamorphoses have been chiefly studied by Strecker. (*Ann. Ch. Pharm.* lxx. 9; lxxvii. 1; lxx. 161 and 166.)



*Preparation.*—1. The precipitate formed in fresh ox-bile is treated with boiling alcohol of 85 per cent., and the liquid is obtained a solution of a lead-salt sufficiently concentrated. The residue is exhausted on the filter with alcohol, and the liquid is then treated with a solution of new precipitates. Sulphydric acid gas is then passed through the solution; the sulphide of lead is separated by filtration; the quantity of water; and the liquid is left at rest as soon as possible. After twelve hours, it is found to be converted into a white precipitate to be washed with cold water.

2. Fresh ox-bile is evaporated to dryness over the water-bath, is coarsely pulverised and treated with cold absolute alcohol. After addition of a small quantity of ether, is left at rest, the bottom of the vessel is found to be covered with a white mass. On decanting the liquid, treating it with fresh alcohol, it at rest, it deposits a considerable quantity of plumose crystals (bile), which go on gradually increasing. The remaining residue after washing with a small quantity of ether, is saturated with ether. The solution is then mixed with water, becomes milky, after which it is left at rest. Twelve hours, it becomes filled with crystals, usually mixed with crystals are thrown on a filter and washed with cold water. The larger product than the former.

Glycocholic acid prepared by either of these methods, a quantity of an isomeric body called *paraglycocholic acid* is obtained. In this admixture, the crystals are washed with cold water; the water: the paraglycocholic acid then remains in the form of glycocholic acid dissolves and crystallises out as the solid.

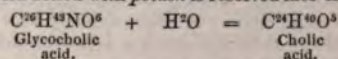
*Properties and Reactions.*—Glycocholic acid crystallises in slender needles, which contract considerably in drying, and form a silky film; 1000 pts. of cold water dissolve 3.3 pts. of it; it dissolves 8.3 pts.; the cold aqueous solution has a saccharine taste, reddens litmus, and is not precipitated by acids, neutral chlorides, or nitrate of silver; but forms a slight precipitate with silver.

Glycocholic acid is easily soluble in alcohol, and the water-bath leaves a residue which is syrupy at first, but on mixing the alcoholic solution with water till it becomes a white emulsion, a quantity of needle-shaped crystals, the liquid becomes clear. The acid is very soluble in ether.

The solutions of glycocholic acid turn the plane of polarisation. The specific rotatory power is  $+27.2^\circ$  for red, and  $+29.9^\circ$  for green light, diminished by combination with alkalis. (F. Hoppe, Chem. Ber., 1860, 1, 100.)

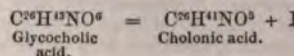
Glycocholic acid dissolves readily in aqueous ammonia, and in baryta-water. The addition of acids, even of acetic, throws down a resinous substance, which changes after a while into a white precipitate. This transformation of the acid is greater rapidly by ether.

Glycocholic acid boiled with potash is resolved into cholonic acid and water.



The same decomposition is produced by baryta-water at 100°. Acetic acid dissolves glycocholic acid, and deposits a white precipitate on evaporation.

Glycocholic acid dissolves easily at common temperature in sulphuric acid, and is precipitated therefrom by water; boiled, it becomes turbid and deposits oily drops of cholesterin after a while:



Glycocholic acid dissolved in water and boiled with cholesterin acid and afterwards dyslysin (p. 360), dyslysin and cholonic acid differ from cholonic acid only by transformation is similar to that produced by boiling potash.

On adding to a solution of glycocholic acid, or an alkaline solution of sugar, then strong sulphuric acid by small portions, applying a gentle heat, a violet or purple colour is produced.



tion of water. This is Pettenkofer's test (see BILL, i. 586). For the application of this test to the detection of biliary acids in the urine, see URINE; also Neukomm (Ann. Ch. Pharm. cxvi. 30).

**Glycocholates.**—The general formula of these salts is  $C^{29}H^{47}MNO^6$ , the acid being monobasic. All the glycocholates are soluble in alcohol; those of the alkali- and earth-metals are easily soluble in water; the rest are sparingly soluble, and may be obtained by precipitation. The solutions of the glycocholates have a sweet and slightly bitter taste.

**Ammonium-salt.**—When dry ammonia-gas is passed into a solution of glycocholic acid in absolute alcohol, in such quantity that no precipitate is formed, needle-shaped crystals separate from the liquid after a while, increasing in number when it is left at rest in closed bottles. The addition of ether accelerates their formation. They lose a considerable quantity of ammonia when kept under an exhausted receiver.

**Barium-salt.**  $C^{29}H^{47}BaNO^6$ .—Glycocholic acid dissolves easily in baryta-water, and on removing the excess of baryta by carbonic acid, then boiling, filtering, and evaporating, glycocholate of barium separates in the form of a white amorphous mass.

The calcium-salt is soluble in water.

The cupric salt is a bluish white precipitate.

The ferric salt forms yellowish flocks, very soluble in alcohol.

The lead-salt is a flocculent precipitate obtained on mixing neutral acetate of lead with an alkaline glycocholate; the precipitation is not however complete, a certain quantity of lead always remaining in solution; it may be completely prevented by adding acetic acid to the solution of the alkaline glycocholate before pouring in the acetate of lead. Basic acetate of lead precipitates sodic glycocholate completely; the precipitate is soluble in alcohol and in excess of acetate of lead.

The magnesium-salt is soluble in water. The potassium-salt closely resembles the sodium-salt.

The silver-salt is obtained as a white gelatinous precipitate on adding nitrate of silver to the solution of an alkaline glycocholate. The precipitate dissolves partially on boiling (completely if the solutions are dilute), and separates again on cooling, in needles if the liquid cools slowly, in the gelatinous form on rapid cooling; but it then becomes crystalline on addition of ether. The salt becomes coloured on exposure to light.

The sodium-salt,  $C^{29}H^{47}NaNO^6$ , constitutes a considerable proportion of ox-bile. It is obtained in the pure state by dissolving glycocholic acid in aqueous carbonate of sodium and evaporating to dryness; or by agitating an alcoholic solution of the acid with effloresced carbonate of sodium, and evaporating off the alcohol. On dissolving the residue in absolute alcohol, and adding ether to the solution, glycocholate of sodium separates in stellate groups of colourless needles, exactly like crystallised bile. It is very soluble in water, less soluble in absolute alcohol, 1000 pts. of alcohol dissolving 15·39 parts of it. When the aqueous solution is evaporated, the salt separates on the edge of the capsule in undulated amorphous crusts; the alcoholic solution behaves in the same manner if evaporated over the water-bath, but yields crystals when very slowly evaporated in a flask. According to Städeler (J. pr. Chem. lxxii. 257) glycocholate of sodium is precipitated in the amorphous state by ether, even from the alcoholic solution of the pure crystallised salt, and more completely in proportion as the alcohol and the ether have been thoroughly freed from water; whence it appears that a certain quantity of water is essential to the crystallisation of the salt. In fact, it separates in a few minutes in very fine stellate groups of needles, without any admixture of the amorphous salt, on adding to the alcoholic solution a sufficient quantity of ether to produce a strong milky turbidity, then dropping in water and stirring till the turbidity just disappears.

Glycocholate of sodium melts when heated, and then burns with a smoky flame, leaving a very fusible cinder, which has an alkaline reaction and contains a large quantity of cyanate.

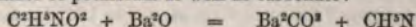
Glycocholate of strontium is soluble in water; consequently the solutions of alkaline glycocholates do not precipitate the solutions of strontium-salts.

**Paraglycocholic acid.** This acid, isomeric with glycocholic acid, constitutes that portion of the precipitate formed by sulphuric acid in crystallised bile, which is insoluble in boiling water; it is composed of nacreous scales, which exhibit under the microscope the form of hexagonal tablets. Similar crystals are found amongst the needles of glycocholic acid crystallised from boiling water; and by dissolving the latter in a fresh portion of boiling water, a certain quantity of the insoluble acid may be separated. It agrees with glycocholic acid in composition (67·10 per cent. C, 9·25 H, 3·01 N, and 20·64 O), and in all its properties, excepting its crystalline form and insolubility in water; it likewise yields salts which are undistinguishable from the glycocholates. It is therefore merely a physical modification of glycocholic acid.





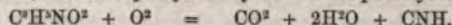
but if the heat be continued, the colour disappears. On adding hydrochloric acid to the residue, hydrocyanic acid is disengaged, and the liquid is found to contain oxalic acid (Horsford). The same fiery-red colour is also produced by heating glycocine with hydrate of barium or oxide of lead. Dilute potash and baryta-water do not eliminate ammonia from glycocine.—3. Glycocine heated with *anhydrous baryta* gives off methylamine (mixed with ammonia), and leaves carbonate of barium.—4. With *hydrate of potassium*, the same products appear to be formed in the first instance, but the methylamine is immediately decomposed into ammonia and free hydrogen, and the residue contains oxalate of potassium as well as carbonate:



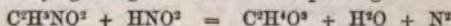
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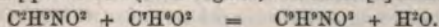
(Cahours, Ann. Ch. Phys. [3] liii. 322; Ann. Ch. Pharm. cix. 29).—5. *Strong sulphuric acid* blackens glycocine when heated with it.—6. When glycocine is heated with a mixture of *dilute sulphuric acid* and *peroxide of lead* or *manganese*, carbonic anhydride is evolved, and the liquid yields by distillation pure hydrocyanic acid:



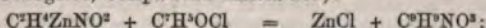
—7. On boiling glycocine with water and peroxide of lead alone, a strong ammoniacal distillate is obtained, and the residue contains carbonate of lead, but no cyanide or formate.—8. It is oxidised by *mercurous nitrate*, the mercury being reduced to the metallic state.—9. *Nitrous acid* converts glycocine into glycollic acid, which may be separated from the liquid by agitating with ether and evaporating:



(Socoloff and Strecker, Ann. Ch. Pharm. lxxx. 18; Dessaignes, Compt. rend. xxxviii. 44).—10. Glycocine boiled for some time with *nitric acid*, or treated with a mixture of *chlorate of potassium* and *hydrochloric acid*, is converted into an acid, which, when saturated with ammonia, yields with chloride of barium a crystalline precipitate, containing, according to Horsford,  $\text{C}^2\text{H}^3\text{Ba}^2\text{O}^7$ . The same acid is produced from glycocine by the action of *chlorine-water*, *nitrous acid* (?) or *permanganate of potassium* (Horsford).—11. *Chlorine gas* immediately attacks the crystals of glycocine, separating water and hydrochloric acid, and producing a hard brown substance partly soluble in water. The acid solution when concentrated deposits large prisms. *Bromine* and *iodine* act like chlorine.—12. Glycocine heated in sealed tubes with *benzoic acid* is converted into hippuric acid (Dessaignes, J. Pharm. [3] xxxii. 44):



Hippuric acid is likewise produced by treating the zinc-salt of glycocine with *chloride of benzoyle* (Dessaignes, Compt. rend. xxxvii. 251):



and by treating the silver-salt of glycocine with *chloride of anisyl*,  $\text{C}^8\text{H}^7\text{O}^2\text{Cl}$ , and *chloride of cumyl*,  $\text{C}^9\text{H}^{11}\text{OCl}$ , acids analogous to hippuric acid are obtained, viz. anisuric acid,  $\text{C}^{10}\text{H}^{11}\text{NO}^3$ , and euminuric acid,  $\text{C}^{12}\text{H}^{13}\text{NO}^3$ .

13. Glycocine mixed in solution with *cyanamide*,  $\text{CN}^2\text{H}^3$ , unites with it, forming glycoeyamine,  $\text{C}^2\text{H}^3\text{N}^2\text{O}^2$ , a compound homologous with creatine (p. 95). (Strecker, Compt. rend. lii. 1212.)

14. According to Braconnot, the aqueous solution of glycocine is not thrown into fermentation by yeast, but according to Buchner (Ann. Ch. Pharm. lxxvii. 203), it is decomposed under the influence of a ferment, and in presence of an alkali, giving off carbonate of ammonium and yielding a number of other products.

**Metallic Compounds of Glycocine.** *Glycollamates* or *Oxyacetamates*.—The general formula of these compounds is  $\text{C}^2\text{H}^3\text{MNO}^2 = \left. \begin{matrix} \text{H}^2 \\ (\text{C}^2\text{H}^3\text{O})^n \\ \text{M} \end{matrix} \right\} \begin{matrix} \text{N} \\ \text{O} \end{matrix}$ .

The *potassium-salt*, obtained by evaporating a solution of glycocine in dilute potash to a syrup over the water-bath, forms alkaline, very deliquescent needles, which must be quickly washed with alcohol. The *barium-salt* is obtained in the crystalline state, by triturating glycocine with hydrate of barium, mixing the semifluid mass with water, and leaving the liquid to evaporate. The remaining salts are obtained by heating the respective oxides with an aqueous solution of glycocine. The *cadmium-salt*,  $2\text{C}^2\text{H}^3\text{CdNO}^2 \cdot \text{H}^2\text{O}$ , forms foliated crystals having a silky lustre. The *copper-salt*,  $2\text{C}^2\text{H}^3\text{CuNO}^2 \cdot \text{H}^2\text{O}$ , is obtained as above; also by treating a mixture of glycocine and sulphate of copper, first with potash and then with alcohol, which precipitates the compound at a certain degree of concentration of the liquid. It forms blue crystals, very soluble in water, not decomposed by carbonic acid. At  $100^\circ\text{C}$ , the crystals give off their water



of crystallisation, amounting to 8 per cent., and turn green obtained by boiling protoxide of lead in aqueous glycocine out of contact of air, forms colourless needles, which are On adding alcohol to the filtrate obtained after boiling colourless needles are formed, resembling cyanide of  $C^4H^2Hg^2N^2O^4.H^2O$ , forms small crystals, the aqueous posed by boiling, metallic mercury being separated, and produced. The *silver-salt*,  $C^2H^4AgNO^2$ , is difficult to Oxide of silver dissolves readily in aqueous glycocine, but the mixture must be digested for some time at  $80^\circ$  to 10 seconds, and filtered at the boiling heat.

**Compounds of Glycocine with Acids and Salts** deduced by direct combination.

*Acetate of Glycocine*,  $2C^2H^3NO^2.C^2H^3O^2.3H^2O$ , is adding alcohol to a solution of glycocine in acetic acid. in water.

*Chromate of Glycocine*. *Chromosaccharic* potassium is deposited in crystals on adding alcohol to an and acid chromate of potassium. It decomposes in a few bonaceous matter, even while immersed in the liquid.

*Hydrochlorates of Glycocine*.—A *monobasic salt*, (boiling hippuric acid with hydrochloric acid. It has an acid, solves very easily in water and in common alcohol, sparing dissolving glycocine in hydrochloric acid, and leaving the hydrochlorate,  $2C^2H^3NO^2.HCl$ , is obtained in crystals below Dominant faces  $\infty P$ ,  $\infty P_2$ ,  $\infty P_\infty$ ,  $P_\infty$ ,  $\frac{1}{2}P_\infty$ ,  $P$ . R erodiagonal and brachydiagonal, = 1 : 1.1108 : 0.3091. I pal section  $\infty P : \infty P = 148^\circ 54'$ ;  $\infty P_2 : \infty P_2 = 12 \frac{1}{2}P_\infty : \frac{1}{2}P_\infty = 131^\circ 32'$ . Cleavage very distinct, parallel *cit.* p. 902). On adding a concentrated solution of dichloride of hydrochloric acid to an aqueous solution of glycocine alcohol drop by drop, cherry-coloured crystals are obtained  $C^2H^3NO^2.HCl.PtCl_3$ .

Glycocine combines with the *chlorides of potassium, sodium, and stannous chloride*. The barium-compound forms crystals rhombic system, with the dominant faces  $\infty P$ ,  $P_\infty$ ,  $\infty P_\infty$ .

*Nitrate of Glycocine*, or *Nitrosaccharic acid*, by carefully evaporating a solution of glycocine in dilute may be purified by recrystallisation. They belong to the faces,  $\infty P$ ,  $\infty P_\infty$ ,  $P_\infty$ ,  $\infty P_\infty$ . Ratio of the principal faces,  $\infty P : \infty P_\infty = 142^\circ 30'$ ;  $\infty P_\infty : \infty P_\infty = 90^\circ$  (Nicklès, *Compt. chim.* 1849, p. 256). The crystals have a bitter taste, somewhat like that of tartaric acid. Nitrate swells up considerably, melts, though not completely, and It does not affect the solutions of the salts of the earth; dissolves iron and zinc with evolution of hydrogen. By slow 2 at. glycocine in 1 at. nitric acid, Dessaignes obtained a barium salt in crystals resembling nitrate of urea.

*Nitrosaccharates*.—These salts are obtained by saturating glycocine with various bases. The *potassium-salt*,  $C^2H^3NO^2$ , salt crystallise in needles sparingly soluble in alcohol. The *lead-salt* is soluble and deliquescent; the *lead-salt* uncrystallisable and crystallisable, and may be obtained by dissolving metallic copper in nitric acid, crystallises in blue needles, by crystallisation and turn green at  $150^\circ C.$ , and decompose at  $182^\circ$ . The *silver-salt*,  $C^2H^3NO^2.NO^2Ag$ , crystallises in needles from the air and alter quickly on exposure to light.

*Oxalate of Glycocine* is obtained by boiling hippuric acid in solution of oxalic acid. The liquid first deposits benzoic acid and then glycocine. The salt forms crystals belonging to the trimorphic system, faces  $\infty P$ ,  $\infty P_\infty$ ,  $\infty P_2$ ,  $P_\infty$ . Ratio of principal and second faces,  $\infty P : \infty P_\infty = 132^\circ$ ;  $\infty P : \infty P_2 = 162^\circ$ ;  $P_\infty : \infty P = 101^\circ 55'$ ;  $P_\infty : P_\infty = 152^\circ 10'$ . (Nicklès, *Compt. chim.* 1849, p. 256).

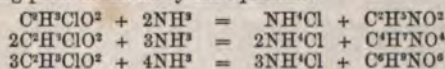
*Sulphate of Glycocine*, or *Sulphosaccharic Acid*, is obtained by saturating glycocine with sulphuric acid.

Obtained by dissolving glycocine in sulphuric acid, in large colourless prisms, which are permanent in the air. They have a sour taste, do not give off anything at 100°, are soluble in water and in warm aqueous alcohol, insoluble in absolute alcohol, and in ether. According to Nicklès (*loc. cit.*), the crystals belong to the trimetric system, with the dominant faces  $\alpha P$ ,  $\alpha \bar{P}\infty$ ,  $\alpha \bar{P}\infty$ ,  $\bar{P}\infty$ . Ratio of principal and secondary axes = 1 : 0.4244 : 0.3207. Inclination of faces,  $\alpha P : \alpha \bar{P}\infty = 125^\circ 10'$ ;  $\alpha P : \alpha \bar{P}\infty = 145^\circ$ ;  $\alpha \bar{P}\infty : \alpha \bar{P}\infty = 90^\circ$ ;  $\alpha P : \bar{P}\infty = 119^\circ 4'$ ;  $\bar{P}\infty : \alpha \bar{P}\infty = 113^\circ$ ;  $\bar{P}\infty : \bar{P}\infty = 138^\circ 20'$ . The composition of this compound has not been satisfactorily determined. Horsford obtained two kinds of crystals, to which he assigned the formulæ  $C^4H^3NO^2.SO^2$ , and  $C^4H^3NO^4.SO^2$ . The formula above given was suggested by Gerhardt. Horsford likewise obtained two basic sulphates, the composition of which is doubtful. Sulphosaccharate of potassium is precipitated in transparent prisms on adding alcohol to an aqueous mixture of glycocine and acid sulphate of potassium.

**Ethylglycocine**,  $C^4H^3NO^2 = C^2H^4(C^2H^3)NO^2$ .—The hydriodate of this base is obtained by heating glycocine with iodide of ethyl and absolute alcohol in sealed tubes. It forms rhombic crystals, which when decomposed by oxide of silver yield the base in small crystals having an alkaline reaction. It forms a crystalline platinum-salt. (Schilling, *Ann. Ch. Pharm.* cxxvii. 97.)

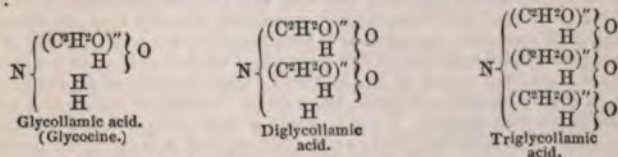
**Dimethyl-glycocine**,  $C^4H^3NO^2 = C^2H^3(CH^3)^2NO^2$ .—The hydriodate of this base,  $C^4H^3NO^2.HI$ , (isomeric with the preceding) is obtained in like manner, together with another hydriodate (probably of methyl-glycocine) the latter crystallising out first. The hydriodate of dimethyl-glycocine crystallises in transparent rhombic prisms. (Schilling, *loc. cit.*)

**Diglycollamic acid**,  $C^4H^3NO^4$ , and **Triglycollamic acid**,  $C^6H^5NO^6$ . (Heintz, *Ann. Ch. Pharm.* cxxii. 257; cxxiv. 297.)—These acids are produced, simultaneously with glycocine (monoglycollamic acid) by the action of ammonia on chloracetic acid, the reactions taking place as shown by the equations:

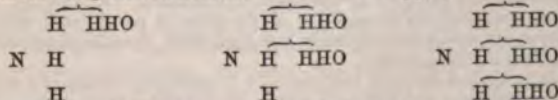


To separate them, the solution obtained by boiling chloracetic acid with ammonia, after being freed from sal-ammoniac by precipitation with alcohol, is boiled with hydrate of lead. A precipitate is then formed consisting of oxychloride and triglycollamate of lead (from which the acid may be separated by sulphuretted hydrogen), and a solution of mono- and di-glycollamate of lead. This solution, after being freed from lead by sulphuretted hydrogen, is boiled with recently precipitated carbonate of zinc, whereby both the acids are converted into zinc-salts, which may be easily separated, the monoglycollamate (zinc-salt of glycocine) being easily soluble in water, while the diglycollamate is very sparingly soluble even at the boiling heat.

Both di- and triglycollamic acids in the free state are crystalline solids, less soluble in water than glycocine, insoluble in alcohol and ether. Their composition and mode of formation show that they are related to glycocine in the same manner as di- and triethylamine are related to ethylamine. The three compounds may be formulated as follows:



these formulæ being derived from the water-ammonia types,



by substitution of the diatomic radical,  $C^2H^3O$ , for the several pairs of bracketed hydrogen-atoms.

Each of these formulæ contains three atoms of hydrogen not included in the radicle  $C^2H^3O$ ; but in the first only one of these hydrogen-atoms belongs to the water-molecule, and is therefore easily replaceable by metals, whereas the second formula contains two, and the third three, hydrogen-atoms thus replaceable: hence glycocine is monobasic, diglycollamic acid is dibasic, and triglycollamic is tribasic.



*Properties.*—Glycogen is a white mealy powder, exhibiting no particular form, even under the microscope. It is neutral, inodorous, and tastes like starch. Dried at  $100^{\circ}\text{C}$ , it contains 44.49 per cent. carbon, 6.49 hydrogen, and 49.02 oxygen (Kekulé), agreeing nearly with the formula  $\text{C}^6\text{H}^{10}\text{O}_5$ , which requires 44.44 C, 6.17 H, and 49.39 O.

Glycogen forms with water an opalescent solution, which, in the absence of ferments, does not undergo spontaneous alteration (Bernard). On evaporating the solution the glycogen separates in films (Hensen). Glycogen is precipitated from its aqueous solution by animal charcoal (Bernard), and according to Bernard and Lehmann, by acetic acid; but according to Gorup-Besanez, this precipitation does not take place, the solution being on the contrary rendered clearer by addition of acetic acid. According to Bernard, it is precipitated from aqueous solution by basic acetate of lead; according to Hensen it is not.

Glycogen is quite insoluble in alcohol (Bernard); slightly soluble. (Hensen.)

Iodine colours it violet or bright brown-red, seldom pure blue (Bernard); violet or most frequently red-brown. (Kekulé.)

*Decompositions.*—1. All reagents which transform starch into sugar, similarly change glycogen, first into a substance corresponding to dextrin, then into sugar (Bernard). The sugar so produced is identical with grape-sugar (Berthelot and de Luca, Compt. rend. xlix. 213). This transformation is occasioned by dilute mineral acids, diastase, and the ferments contained in the blood, saliva, liver, and pancreas (Bernard). Boiling dilute sulphuric acid first clarifies the aqueous solution, and only produces sugar after continued boiling (Kekulé).—Neutral aqueous glycogen is immediately converted into sugar by saliva; the transformation takes place very slowly, or not at all, in presence of free acid, caustic alkalis, or alkaline carbonates (Pavy). If the glycogen contained in a concentrated decoction of liver or muscular flesh is warmed with saliva, it ferments on the subsequent addition of yeast (Poggiale). Glycogen which has not undergone this preliminary treatment does not ferment on addition of yeast. (Bernard.)

2. By roasting, glycogen is converted into a substance similar to dextrin (Bernard). The dextrin formed thus, or according to 1, rotates the plane of polarisation towards the right, does not reduce an alkaline cupric solution, is not coloured blue by iodine, and does not ferment with yeast. It gives a clear solution with water, not with strong alcohol. (Bernard.)

3. Glycogen yields xyloïdin when treated with concentrated nitric acid; and oxalic acid when boiled with dilute nitric acid (Pelouze). If concentrated nitric acid is poured over glycogen dried at  $100^{\circ}\text{C}$ ., solution takes place after a few moments, and, if water is immediately added, a quantity of xyloïdin is obtained amounting to 130 per cent. of the glycogen employed. If the nitric acid solution is allowed to stand for some time, water precipitates a smaller quantity of xyloïdin, and after several days none at all (Pelouze).—4. Glycogen does not reduce an alkaline solution of a cupric salt. (Bernard.)

*Physiological relations.*—The function of glycogen in the animal economy is a subject on which the opinions of physiologists are much divided. Bernard, who discovered it, maintains, that it is converted into sugar in the liver, by the action of a ferment contained in that organ, and that this conversion of glycogen into sugar is a constant and normal function of the liver. This view is founded on the observation, made by Bernard himself and others, that in carnivorous animals the blood of the portal vein is quite free from sugar, whereas that of the hepatic veins contains a considerable quantity of it; and that in herbivorous and omnivorous animals the amount of sugar in the hepatic veins is always much greater than in the portal vein. Lehmann (Compt. rend. xl. 228) found that the portal blood of dogs which had been kept fasting or fed entirely on meat was free from sugar, whereas that of the hepatic vein contained a quantity amounting to between 0.6 and 0.9 per cent. of the dried residue of the blood. When the dogs were fed on potatoes, the portal blood contained only traces of sugar, the blood of the hepatic vein from 0.8 to 1 per cent. (of the dry residue). The portal blood of horses fed on bran, hay, and straw, contained 0.05 per cent. sugar, that of the hepatic vein from 0.6 to 0.9 per cent. (of the dry residue). Lehmann also found that in the passage of the blood through the liver, the fibrin disappears altogether and the albumin in great part; and he supposed that the sugar in the liver was formed from the fibrin of the blood. Harley (Proc. Roy. Soc. x. 297) obtained results similar to those of Bernard and Lehmann, with regard to the presence or absence of sugar in the portal blood according to the nature of the diet; he also finds that sugar is a normal constituent of the blood of the general circulation; that the livers of dogs contain sugar whether the diet is animal or vegetable, and that, under favourable circumstances, sugar may be found in the liver of an animal after three entire days of rigid fasting; and he concludes that the sugar found in the bodies of animals fed on a



mixed diet is partly derived from the food, partly formed in the liver; that the livers of animals restricted to flesh diet possess the power of forming glycogen, which glycogen is at least partly transformed into sugar; and that, as sugar is found in the liver at the moment of death, its presence cannot properly be ascribed to a *post mortem* change, but is to be regarded as the result of a natural condition.

On the other hand, Figuier, Pavy, and others find that the blood, after leaving the liver does not, under normal conditions, contain a larger amount of sugar than before entering that organ. According to Pavy, blood collected from the right side of the heart during life (by catheterism) contains but a trace of sugar, although when collected from the same part after death, it gives abundant indication of the presence of that substance. The heart excised instantaneously after sudden killing, contains blood as free from sugar as during life. Pavy also concludes from his own experiments, that the saccharine state of the liver, which has hitherto been looked upon as belonging to life, is the result of a *post mortem* change which takes place with astonishing rapidity. The glycogen (or heptatin) in the liver is in contact with a ferment capable under certain circumstances of transforming it into sugar, but this transformation does not take place during life, and moreover may be checked by the influence of acids, alkalis, extreme cold, and a heat sufficient to destroy and coagulate the ferment; and by means of these agencies it may be shown that if the liver contains any sugar at the moment of death, it is only to the extent of the merest trace. Carbonate of sodium injected into the portal system during life causes a rapid disappearance of glycogen from the liver without any sign of the production of sugar. The livers of animals naturally of low temperature, such as the frog, oyster, and mussel, are free from sugar during life and at the time of death.

The ingestion of starch and saccharine substances leads to a great accumulation of glycogen in the liver, that organ at the same time increasing greatly in size. The average weight of the liver of eleven dogs fed on animal diet was  $\frac{35}{100}$  of that of the animal, and an analysis of seven of the livers gave an average percentage of glycogen amounting to 7.19. Five dogs fed upon a vegetable diet gave an average weight of liver equal to  $\frac{15}{100}$  of that of the animal. An analysis of three of the livers gave an average percentage of glycogen amounting to 17.23. Four dogs fed upon a diet of animal food with a large admixture of sugar, gave an average weight of liver equal to  $\frac{1}{16.5}$  of that of the animal, with a percentage of glycogen amounting to 14.5. Similar results were obtained by experiments upon rabbits, showing that saccharine and amylaceous matters received as food are converted in the liver into glycogen. Pavy regards this fact as affording a strong argument against the supposition that sugar is formed in the liver during life, as it appears highly improbable that sugar should be first transformed by the liver into glycogen, in order to be reconverted into sugar in the same organ.

M'Donnell regards glycogen as the basis of an azotised protoplasm forming a constituent of blood. For if it be true—as appears from the observations of Lehmann, Brown-Séquard, and also of M'Donnell—that the fibrin and much of the albumin of the portal blood vanishes in the liver, and that the liver, at the same time that it destroys these azotised compounds, forms its own non-azotised amyloid substance, and excretes bile containing so little nitrogen that it need hardly be taken into account, the conclusion seems obvious that “the nitrogen, which leaves the liver by no other outlet, may go forth in the hepatic blood in union with the amyloid substance, thus changed into a new azotised principle; that thus the liver is a great blood-making organ, in which there is constantly going on a reconstruction of certain ingredients of the blood; that in it, the fibrin, &c., which has done its work, is disintegrated, the hydrocarbons of the bile abstracted, and the nitrogen combined with the amyloid substance, which instead of being normally changed into sugar, emerges from the liver, as a constituent principle of the protoplasm, from which (to use the words of Bernard with reference to the fetal tissues) organic evolution is accomplished.”

**GLYCO-HYOCHOLIC ACID.** See HYO-GLYCOCHOLIC ACID.

**GLYCOL, AMYLENIC.** See AMYLENE, HYDRATE OF (i. 208).

**GLYCOL.** See ETHYLENE, HYDRATES OF (p. 574).

**GLYCOLALDYL.** The name given by Heintz (Pogg. Ann. cxi. 165, 291) to a diatomic radicle,  $C^2H^2$ , which he supposes to exist in oxalic and saccharic acids.

**GLYCOLIC ETHERS.** The ethers of the diatomic alcohols or glycols (p. 517); not to be confounded with glycollic ethers, the ethers of glycollic acid.

**GLYCOLLAMIDE.**  $C^2H^2NO = \left( \begin{array}{c} H \\ C^2H^2O \end{array} \right)^N \begin{array}{c} O \\ N \end{array}$ .—This compound, isomeric with glycocine, is produced:—1. By dissolving glycollicide in aqueous ammonia.—2. By the action of ammonia on glycollate of ethyl (Heintz).—3. By the action of heat on

tartrate of ammonium:  $C^2H^3(NH^4)O^2 = C^2H^3NO^2 + CO^2 + H^2O$ . This salt melts at  $150^\circ C$ . with violent evolution of carbonic anhydride; on continuing the heat, carbonate of ammonium escapes, and at length there remains a residue which solidifies on cooling, and when recrystallised from water yields beautiful crystals of glycollamide. (Dessaigues, *Compt. rend.* xxxviii. 47.)

This substance dissolves readily in water, and sparingly in alcohol, and may be recrystallised from boiling alcohol, differing in this respect from glycocine, which is nearly insoluble in alcohol. It has a faint, somewhat sweetish taste, and slight acid reaction (Dessaigues). According to Heintz, it is neutral, melts at  $120^\circ C$ ., without decomposition, and does not unite with bases (glycocine melts with partial decomposition at  $170^\circ$  and forms salts with bases). It is not decomposed by potash in the cold; but when boiled with potash, it yields ammonia and glycollate of potassium, in which respect also it differs from glycocine (p. 903). It is decomposed in a similar manner by aqueous acids. Heated to  $100^\circ C$ . in a current of dry hydrochloric acid gas, it unites directly with the acid, forming a thick liquid, which crystallises on cooling, provided the action has not been too long continued; but at a higher temperature it is decomposed, yielding sul-ammoniac and glycollide. (Heintz, *Ann. Ch. Pharm.* cxxiii. 212.)

**GLYCOLLIC ACID.**  $C^2H^4O^3 = \left( \begin{smallmatrix} H \\ C^2H^2O \\ H \end{smallmatrix} \right) \left\{ \begin{smallmatrix} O \\ O \end{smallmatrix} \right.$ . Oxacetic acid. (Socoloff and

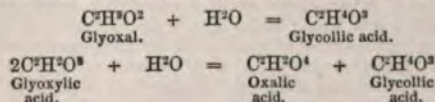
Strecker, *Ann. Ch. Pharm.* lxxx. 18.—Dessaigues, *Compt. rend.* xxxviii. 44.—Kekulé, *Ann. Ch. Pharm.* cv. 286.—*Gm.* xii. 508; xiii. 435.—*Gerh.* i. 222; ii. 930.—Schulze, *Zeitschr. Ch. Pharm.* 1862, pp. 606, 682.—Drechsel, *Ann. Ch. Pharm.* cxxvii. 150.)

*Formation and Preparation.*—1. Benzoglycollic acid,  $C^7H^3(C^2H^3O)O^2$ , is resolved by boiling with water to which a little sulphuric acid is added, into glycollic and benzoic acids: the greater part is decomposed in the course of a few hours, but to render the decomposition quite complete, several days' boiling is required. The liquid is evaporated as long as benzoic acid continues to separate on cooling, then neutralised with carbonate of barium, filtered from the resulting sulphate of barium, and evaporated to a syrup. The barium-salt, which crystallises out on cooling, is dissolved in a small quantity of water, and decomposed by dilute sulphuric acid; the filtered solution evaporated to a syrup; this residue dissolved in ether; and the ethereal solution left to evaporate. (Socoloff and Strecker.)

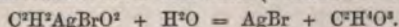
2. An aqueous solution of glycocine is decomposed by nitrous acid with evolution of nitrogen gas (p. 903); and the liquid mixed with ether and evaporated leaves glycollic acid. If the liquid is evaporated immediately after the action of the nitrous acid, the glycollic acid thus produced is converted into oxalic acid. (Socoloff and Strecker.) Dessaigues, by the same process, obtained glycollic acid in the crystalline form.

3. Tartaric acid,  $C^4H^4O^6$ , is heated to  $180^\circ C$ ., till no more gas is evolved; the residue, consisting of nearly pure glycollide, is washed with cold water and dissolved in potash; the resulting glycollate of potassium is precipitated by nitrate of silver, and the glycollic acid is separated from the silver-salt by hydrochloric acid. (Dessaigues.)

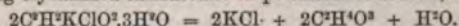
4. By the action of alkalis on glyoxal or glyoxylic acid (Debus):



5. By boiling bromacetate of silver with water (Perkin and Duppa, i. 665):



By boiling iodoacetic acid with oxide of silver, or iodoacetate of lead with water, or by decomposing the solution of that salt with sulphydric acid (Perkin and Duppa, *Phil. Mag.* [4] xviii. 54). In like manner, by boiling chloroacetic acid with caustic alkalis, or heating crystallised chloracetate of potassium or sodium, *e. g.*:



Chloracetate of potassium, heated to  $100^\circ$ — $120^\circ C$ . becomes moist, and acquires an acid reaction; and if the heat be continued till the mass becomes dry, and the residue digested with ether-alcohol, glycollic acid dissolves and may be obtained by evaporation as a yellowish syrup. It may be obtained colourless by prolonged boiling of the concentrated solution of the chloracetate of potassium, or by heating the crystallised salt in a closed tube for several hours to  $120^\circ$ — $140^\circ C$ . The acid thus prepared does not crystallise; but by decomposing chloracetate of silver with sulphydric acid, and



evaporating the filtrate to a syrup, glycollic acid is obtained in radiate groups of large very deliquescent crystals. (Kekulé, *Ann. Ch. Pharm.* cv. 286.)

6. When glycol ( $C^2H^4O^2$ ) is dissolved in four times its bulk of nitric acid of specific gravity 1.33, and the solution, after standing for several days, is concentrated in vacuo over quick-lime, an acid syrupy residue is left, which, when dissolved in water, neutralised with chalk, and mixed with alcohol, yields a precipitate of glycollate of calcium, and on precipitating the calcium by the exact quantity of oxalic acid required, and evaporating the filtrate in vacuo, glycollic acid is obtained in crystals (Wurtz *Compt. rend.* xlv. 1306; *Ann. Ch. Pharm.* cii. 366). Glycollic acid is also formed together with other products, when tritylene-glycol,  $C^6H^8O^2$ , is oxidised by nitric acid and in small quantity—lactic acid being the chief product—when air is slowly passed over a mixture of platinum-sponge and platinum-black moistened with tritylene-glycol (Wurtz, *Compt. rend.* xlv. 306).

7. Glycollic acid is produced, together with glyoxal, glyoxylic acid and other products, by the action of nitric acid upon alcohol (Debus, see page 922). A quicker mode of preparation is given by Lautemann (*Kolbe's Org. Chem.* i. 678). A few grammes of strong alcohol are gently heated in a capacious vessel, with a small quantity of nitric acid, till the vessel becomes filled with red fumes of nitrous acid; and when the action has been thus set up, about 500 grms. alcohol of 20 per cent., and 440 grms. nitric acid of specific gravity 1.34 are poured in. The reaction, which must be moderated by immersing the vessel in water at  $20^\circ C$ , is complete in about 12 hours. The glycollic acid may then be separated from the other products in the form of a calcium-salt by Debus's method (see GLYOXYLIC ACID, p. 922).—Drechsel dissolves the mixture of glycollate of calcium, glyoxal and glyoxylate of calcium in boiling water, and boils it for several hours with milk of lime, whereby both the glyoxal and the glyoxylic acid are converted into glycollic acid. The hot filtrate freed from excess of lime by carbonic acid yields tolerably pure glycollate of calcium; and by decomposing this salt with oxalic acid, neutralising the filtrate with carbonate of lead, and evaporating, the neutral glycollate of lead is obtained in well developed crystals. The hot aqueous solution of this salt, decomposed by an equivalent quantity of dilute sulphuric acid, yields a solution of glycollic acid, which may be crystallised by evaporation to a syrup at  $60^\circ$  or  $70^\circ C$ , afterwards in vacuo over oil of vitriol, and purified by recrystallisation from anhydrous ether.

In the mother-liquor obtained in the preparation of fulminating mercury (p. 732), Cloez (*Compt. rend.* xxxiv. 864) found an uncrystallisable acid (which he called *Homolactic acid*) having the composition of glycollic acid.

8. By the action of nascent hydrogen upon oxalic acid,  $C^2H^2O^4 + H^2 = C^2H^4O^3 + H^2O$  (Schulze). An aqueous solution of oxalic acid is boiled with sulphuric acid, and excess of zinc powder gradually added as long as hydrogen continues to escape; the filtrate is neutralised with lime, &c. as above; the calcium-salt is converted into a basic lead-salt by precipitation with neutral acetate of lead; and from this salt the free acid is prepared. According to Church, glyoxylic acid is produced in this reaction, as well as glycollic acid, and afterwards converted into glycollic acid by boiling with lime (see No. 4). A larger quantity of glycollic acid may be at once produced by conducting the process so as to increase the energy of the reducing action as much as possible. With this view, Church adds oxalic acid in successive small portions to a large quantity of zinc and sulphuric acid heated over a lamp; keeps up a brisk evolution of hydrogen for some hours; boils the liquid with excess of zinc till all the acids present are saturated; then adds excess of lime, saturates the whole with carbonic acid, boils, and filters. The filtrate on concentration deposits abundance of glycollate of calcium in concentric tufts of fine needles. The mother-liquor contains a peculiar acid, isomeric with acetic acid.

9. By the action of nitric acid upon acrolein (Claus, *Ann. Ch. Pharm. Suppl.* ii. 119).—10. By the action of boiling water on the brominated oil obtained by treating anhydrous glycerin with bromine. (Barth, p. 890.)

*Properties.*—Glycollic acid appears to exist in two, if not in a greater number of isomeric modifications. The acid which Socoloff and Strecker obtained from hippuric acid, and that found by Cloez in the mother-liquor of the preparation of fulminate of silver, were syrupy and uncrystallisable. All the other processes above given yield crystallisable acids; but those obtained by Dessaignes from glycocine and from tartaric acid, and that which Kekulé prepared from chloracetic acid, were extremely deliquescent, whereas Drechsel's acid, prepared by the action of nitric acid on alcohol, deliquesces only in very damp air. This acid exhibits the following properties. It crystallises from anhydrous ether by slow evaporation in beautiful regular crystals; has a very sour taste; dissolves easily in water, alcohol and ether; is permanent in dry or in moderately damp air, but deliquesces in very damp air, the deliquesced mass crystallising again in regular crystals on being removed to a dry atmosphere. It melts at  $78^\circ$  or  $79^\circ C$ , and after cooling remains liquid for some time, but solidifies in the



crystalline form on being touched with a pointed body. When heated in a retort, the fused acid begins to boil at  $100^{\circ}\text{C}$ ., aqueous glycollic acid passing over as the temperature continually rises. Above  $150^{\circ}$  it gives off extremely pungent vapours, and yields an oily distillate, which on exposure to the air gradually solidifies to a deliquescent crystalline magma. The acid obtained by reduction of oxalic acid behaves in a similar manner, but does not begin to decompose till heated above  $180^{\circ}\text{C}$ . (Schulze.)

The acid prepared from alcohol, when kept for some time in the fused state at the temperature of the water-bath, gradually loses its property of recrystallising, and is ultimately converted into an uncrystallisable syrup containing a higher percentage of carbon than pure glycollic acid, and consisting probably of a mixture of that acid with glycolide. The syrupy acid thus produced can only be partially brought back to the crystallisable state by boiling with water, and forms with bases, salts which differ in some respects from those of the crystalline acid. (See below.)

**GLYCOLLATES.**—Glycollic acid is diatomic but monobasic (like lactic acid) only one of its typic hydrogen-atoms being *saline*, that is, replaceable by metals. The other is *alcoholic*, that is to say, more easily replaced by acid-radicles, as in benzoglycollic acid (see GLYCOLLIC ETHERS, p. 915). This difference between the hydrogen-atoms may be conveniently represented in the rational formula, by writing the alcoholic H above, and the saline H below. The general formula of the metallic glycollates will

then be  $\begin{matrix} \text{H} \\ \text{C}^2\text{H}^2\text{O} \end{matrix} \begin{matrix} \text{O} \\ \text{O} \end{matrix}$ ; that of benzoglycollic acid,  $\begin{matrix} \text{C}^2\text{H}^2\text{O} \\ \text{H} \end{matrix} \begin{matrix} \text{O} \\ \text{O} \end{matrix}$ .

*Glycollate of Ammonium* (with excess of acid),  $\text{C}^2\text{H}^2(\text{NH}^4)\text{O}^2.\text{C}^2\text{H}^2\text{O}^2$ .—This salt is obtained by repeatedly evaporating a solution of glycollic acid in ammonia; also by evaporating the mother-liquor which remains in the preparation of glycolamide (p. 908), by the action of ammonia on acid glycollate of ethyl. It crystallises in concentric groups of slender needles, which are easily soluble in water and in boiling alcohol, have a strong acid reaction, and cannot be dried at  $100^{\circ}$ — $110^{\circ}\text{C}$ . without decomposition. (Heintz.)

*Glycollate of Barium*,  $\text{C}^2\text{H}^2\text{BaO}^2$ , separated from a moderately concentrated solution, forms large transparent crystals; if the solution be evaporated to a syrup the salt separates in crystalline crusts (Kekulé). It melts when heated, forming a clear liquid, which crystallises on cooling. At a stronger heat it is decomposed, leaving carbonate of barium. Dissolves in 7.91 pts. water at  $17^{\circ}\text{C}$ . (Schulze.)

*Glycollate of Calcium*,  $\text{C}^2\text{H}^2\text{CaO}^2$ , obtained by boiling the dry acid with lime-water, removing the excess of lime by carbonic acid, and concentrating, separates on cooling in stellate groups of asbestos-like needles. It dissolves sparingly in cold water, but sufficiently to give a precipitate with alcohol. The crystals contain water,  $\frac{2}{3}$  at. according to Schulze, which they give off at  $100^{\circ}\text{C}$ . At a higher temperature the salt burns away, leaving carbonate of calcium (Kekulé). Debus, by neutralising glycollic acid with chalk, precipitating with alcohol, and recrystallising from water, obtained crystals containing  $\frac{2}{3}$  at. water,  $2\text{C}^2\text{H}^2\text{CaO}^2.3\text{H}^2\text{O}$ , which they gave off at  $100^{\circ}$ , or a little above. A double salt of *glycollate* and *glyoxylate* of calcium,  $\text{C}^2\text{H}^2\text{CaO}^2.2\text{C}^2\text{H}^2\text{CaO}^2.\text{H}^2\text{O}$ , crystallises from the mother-liquors obtained in the preparation of glyoxylic acid (p. 922).

*Glycollates of Lead*.—The *neutral salt* crystallises from a solution of the basic salt in free glycollic acid, in beautiful shining monoclinic crystals resembling those of gypsum. It dissolves in about 31 pts. water at  $17^{\circ}\text{C}$ ., but is decomposed at the same time into the basic salt, which is precipitated, and free glycollic acid (Schulze).—The neutral lead-salt prepared from crystalline glycollic acid (by neutralising it with carbonate of lead) crystallises in monoclinic prisms, exhibiting the faces  $\alpha\text{P}$ ,  $\alpha\text{P}\infty$ ,  $\text{oP}$ . Inclination of clinodiagonal to principal axis =  $82^{\circ} 36'$ ;  $\alpha\text{P} : \alpha\text{P} = 78^{\circ} 6'$ ;  $\alpha\text{P} : \alpha\text{P} = 129^{\circ} 10'$ ;  $\text{oP} : \alpha\text{P} = 94^{\circ} 40'$ ;  $\text{oP} : \alpha\text{P}\infty = 97^{\circ} 94'$ ; they are sometimes short prisms, sometimes tabular from predominance of  $\alpha\text{P}\infty$ . Dissolves in 33.1 pts. water at  $15^{\circ}\text{C}$ . The lead-salt prepared from the syrupy acid has the same composition, but forms pointed crystals which appear as if they belonged to the trimetric system, but the faces were too much striated and curved to admit of exact angular measurement. Soluble in 35.9 pts. water at  $15^{\circ}\text{C}$ . (Drechsel.)

A *basic lead-salt*,  $\text{Pb}^2\text{O}.2\text{C}^2\text{H}^2\text{PbO}^2$ , is obtained by precipitating a solution of the calcium-salt in not more than 100 pts. water with neutral acetate of lead, the neutral salt being probably formed in the first instance, and then decomposed by the water as is above mentioned; with basic acetate of lead it is produced more quickly and in greater quantity. It is crystalline, requires more than 10,000 pts. cold, and nearly as much hot water to dissolve it; but is easily soluble in free acetic acid, and in acetate of lead, whether neutral or basic. (Schulze.)

*Glycollate of Magnesium* separates from aqueous solution by slow evaporation

in nodular groups of hydrated needles and laminae. It does not swell up when heated (Schulze.)

**Glycollate of Silver,**  $C^2H^3AgO^3$ , separates on mixing a hot aqueous solution of the calcium-salt with nitrate of silver, and leaving the liquid to cool—in spangles the solution is rather strong, in laminae from weaker solutions. It dissolves sparingly in cold water, is decomposed by boiling with water, and is insoluble in alcohol (Kekulé). Dessaignes, by mixing a solution of glycollide in potash with nitrate of silver, obtained a precipitate which soon became crystalline, dissolved readily in hot water, and separated therefrom in large crystals having the composition of glycollate of silver containing water:  $C^2H^3Ag^2O^5 + H^2O$ .

The silver-salt prepared from crystalline glycollic acid crystallises easily, and with great beauty; that from the syrupy acid decomposes very quickly. (Drechsel.)

**Glycollate of Zinc,**  $C^2H^3ZnO^3.H^2O$ , crystallises in tufts of needles or prisms which give off their water at  $100^\circ C$ . When the salt in excess is shaken up with water at  $17^\circ C$ ., a solution is formed, containing 1 pt. of the anhydrous salt in 31.6 pt. water; but in hot water supersaturated solutions are formed, which after cooling to  $17^\circ$  may contain as much as 1 pt. of the salt in 26.14 pts. water. (Schulze.)

The crystalline acid yields a zinc-salt which crystallises in well developed needles the syrupy acid, a salt which forms microscopic four- or six-sided tablets. Both require 34 pts. water at  $15^\circ C$ . to dissolve them. (Drechsel.)

#### Derivatives of Glycollic acid.

**Acetoglycollic acid.**  $C^4H^6O^4$ . See ACETOGLYCOLLATE OF ETHYL (p. 917).

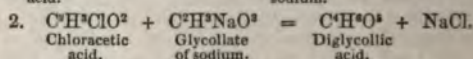
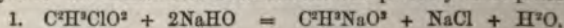
**Benzoglycollic acid.**  $C^9H^8O^4$ . (See vol. i. p. 548.)

**Bromoglycollic acid.**  $C^2H^3BrO^3 = \left( \frac{C^2HBrO}{H} \right)^2 O^2$ . (Perkin and Duppé, Chem. Soc. Qu. J. xii. 5.)—Produced by boiling dibromacetate of silver with water:



It forms a silver-salt which, when heated with water, yields bromide of silver and glyoxylic acid,  $C^2H^2O^3$  (p. 922):  $C^2H^3AgBrO^3 + H^2O = AgBr + C^2H^2O^3$ .

**Diglycollic acid.**  $C^4H^4O^5 = \left( \frac{C^2H^2O^3}{H} \right)^2 O^2$ . *Paramalic acid.*—This acid, which is isomeric with malic acid, and stands to glycollic acid in the same relation as diethylene to monoethylenic alcohol, is produced by the dehydration of glycollic acid,  $2C^2H^3O^3 - H^2O = C^4H^4O^5$ , and by the oxidation of diethylenic and triethylenic alcohols. It was discovered by Heintz (Pogg. Ann. cix. 470; Jahresb. 1859, p. 362) who obtained it in preparing glycollic acid by heating chloracetate of sodium with caustic soda, and gave it the name of *paramalic acid*. Wurtz soon afterwards obtained an acid of the same composition, which he called *diglycollic acid*, by oxidising diethylenic alcohol with nitric acid or with platinum-black (Compt. rend. li. 162; Jahresb. 1860, p. 444); and Heintz subsequently showed (Pogg. Ann. cxv. 280, 452; Jahresb. 1861, p. 440) that the acids obtained by these two methods are identical. It is also produced by heating glycollic acid to  $200^\circ - 240^\circ C$ ., but the greater part of it then suffers further decomposition, yielding glycollide,  $C^2H^2O^2$ , and a small quantity of dioxyethylene. Its formation from chloracetic acid probably takes place thus:



**Preparation.**—1. *From Chloracetic acid.* The acid, mixed with a large quantity of water is [slightly] supersaturated with slaked lime and the solution is boiled till it again exhibits an acid reaction; more lime is then added, and this treatment is repeated till the alkaline reaction no longer disappears, even after prolonged boiling. The excess of lime is then precipitated from the boiling liquid by carbonic acid, and the solution is filtered; it then on cooling deposits a considerable quantity of diglycollate of calcium in colourless crystals. The liquid filtered from this deposit yields by evaporation, after the chloride of calcium contained in it has been extracted by absolute alcohol, a residue which still contains diglycollate of calcium, together with a small quantity of glycollate, from which it may be freed by recrystallisation, the diglycollate being much the less soluble of the two. The diglycollate of calcium, boiled with a mixture of ammonia and carbonate of ammonium, yields the acid ammonium-salt, and the solution of this salt saturated with ammonia and mixed with



acetate of lead, yields a precipitate of diglycollate of lead, from which the acid may be obtained by decomposition with sulphuretted hydrogen. (Heintz.)

2. *By oxidation of Diethylenic alcohol.*—Diethylenic alcohol is violently attacked by nitric acid, with copious evolution of red fumes. The acid liquid when evaporated solidifies to a crystalline mass; and by dissolving this residue in water, saturating with milk of lime, heating to the boiling point, filtering to separate oxalate of calcium, filtering again and leaving the filtrate to cool, diglycollate of calcium is obtained in long shining needles. The boiling aqueous solution of this salt mixed with nitrate of silver yields a precipitate of diglycollate of silver; and this, decomposed by sulphuretted hydrogen, yields diglycollic acid. (Wurtz.)

A liquid containing nitrate of silver and milk-sugar used in photography for dipping papers impregnated with succinic acid, citric acid, &c. has been found, after long usage, to deposit a silver-salt isomeric with malate and diglycollate of silver (Kämmerer, J. pr. Chem. lxxxviii. 321; Rép. Chim. pure, 1863, p. 370). The acid obtained from this salt, called by its discoverer isomalic acid, is perhaps identical with diglycollic acid; but the identity is not quite established. (See ISOMALIC ACID.)

*Properties.*—Diglycollic acid crystallises in thick rhombic prisms containing  $C^4H^4O^4.H^2O$  (Wurtz); in monoclinic prisms (Heintz). It has a very sour taste, is inodorous, and has no action on polarised light (Heintz). The crystals give off their water slowly in the air at ordinary temperatures, quickly in vacuo or at  $100^\circ C.$ ; they dissolve easily in water and in alcohol, sparingly in ether. The dry acid melts at  $148^\circ C.$ , and solidifies in the crystalline form on cooling. Between  $250$  and  $270^\circ C.$  it decomposes, giving off a gaseous mixture containing but little carbonic anhydride, burning with a blue flame, and leaving a residue which, when distilled over the open fire, yields a thick strongly acid liquid, which after a while solidifies to a crystalline mass.

*DIGLYCOLLATES.*—Diglycollic acid is dibasic, forming *neutral salts*,  $C^4H^4M^2O^4$ , and *acid salts*,  $C^4H^4MO^4$ . The neutral diglycollates of the alkali-metals are easily soluble in water; the rest are sparingly soluble, and may be obtained by precipitation. The solution of the free acid is not precipitated by *lime-water*, but gives precipitates after a while with *bariata-* and *strontia-water*. Nitrate of silver precipitates it only on addition of ammonia; the precipitate is soluble in excess of ammonia, but separates out unaltered on boiling the solution. The solution of the ammonium-salt immediately forms white precipitates with nitrate of silver and mercurous nitrate; white crystalline precipitates after a while with acetate of lead and sulphate of zinc; blue crystalline with sulphate of copper; and reddish crystalline with nitrate of cobalt.

*Diglycollate of Ammonium* (acid),  $C^4H^4(NH^1)^4O^4$ , obtained by boiling the calcium-salt with ammonia or carbonate of ammonium, then filtering and evaporating, forms long monoclinic prismatic crystals, insoluble in common alcohol, very sparingly soluble in boiling absolute alcohol (Heintz). The neutral *ammonium-salt* has not been obtained pure.

*Diglycollate of Barium*,  $C^4H^4Ba^2O^4.H^2O$ .—Obtained by precipitating the solution of a neutral alkaline diglycollate with chloride of barium, as a white crystalline precipitate, sparingly soluble in cold water, insoluble in alcohol. It must be recrystallised to free it from chloride of ammonium and excess of chloride of barium, which adhere to it somewhat obstinately, and cannot be removed by washing. (Heintz.)

*Diglycollate of Calcium*,  $C^4H^4Ca^2O^4.6H^2O$ , prepared as above described, crystallises in long shining needles, nearly insoluble in cold, sparingly soluble in boiling water. It gives off its water at  $160^\circ C.$  (Wurtz), at  $180^\circ C.$  (Heintz.)

*Diglycollate of Copper*,  $C^4H^4Cu^2O^4$ .—Blue, sandy, slightly crystalline precipitate, which dissolves slowly in water, taking up at the same time a certain quantity, which may be expelled to the amount of 3 per cent. at  $180^\circ C.$  The undried salt probably contains  $2C^4H^4Cu^2O^4.H^2O$ . (Heintz.)

*Diglycollate of Lead*,  $C^4H^4Pb^2O^4$ , obtained by precipitation, as above described, forms white microscopic crystals, which dissolve sparingly in water, easily in nitric and in hydrochloric acid, and begin to decompose with slight coloration at  $200^\circ C.$  (Heintz.)

*Diglycollate of Magnesium*,  $C^4H^4Mg^2O^4.3H^2O$ , obtained by saturating the aqueous acid with magnesia, forms small prismatic crystals, which do not give off their water till heated above  $200^\circ C.$ ; the anhydrous salt is not decomposed at  $240^\circ$ . (Heintz.)

*Diglycollates of Potassium.*—The *acid salt*,  $C^4H^4KO^4$ , is sparingly soluble in water, and separates in crystals when one-half of a strong solution of the acid is neutralised with potash, and then mixed with the other half (Wurtz). The crystals are trimetric combinations,  $\infty P . \infty P . \bar{P} \infty$ . Inclination of  $\infty P : \infty P = 112^\circ 64'$ ;



$\bar{P} \infty : \bar{P} \infty$  over the principal axis =  $118^{\circ} 30'$  (Heintz). The solution left to stand in an open vessel becomes covered with mould. The salt blackens when heated, giving off the odour of burnt sugar (Wurtz). The *neutral salt*,  $C^4H^4K^2O^2$ , obtained by neutralising the free acid or the preceding salt with potash, crystallises in long deliquescent needles. (Heintz.)

*Diglycollate of Silver*,  $C^4H^4Ag^2O^2$ , is obtained as a white granular precipitate on adding nitrate of silver to a boiling saturated solution of the calcium-salt. (Wurtz.)

*Diglycollates of Sodium*.—The *acid salt*,  $C^4H^2NaO^3$ , forms small tabular crystals, sparingly soluble in water, but more soluble than the acid potassium-salt. The *neutral salt* is not deliquescent; it is insoluble in alcohol even at the boiling heat. (Heintz.)

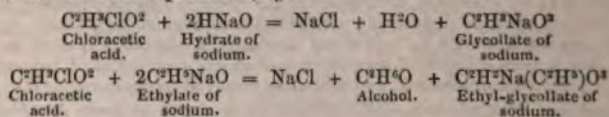
*Diglycollate of Sodium and Potassium*,  $C^4H^4KNaO^3.2H^2O$ , obtained by exactly saturating the acid potassium-salt with soda, forms small tabular prismatic crystals, which have a nacreous lustre, are insoluble in alcohol, and melt in their water of crystallisation at  $100^{\circ} C$ . An *ammonio-sodic* salt has been obtained, but not in the pure state. (Heintz.)

*Diglycollate of Strontium*,  $C^4H^4Sr^2O^2.H^2O$ , resembles the barium-salt, and is prepared in a similar manner, but is more easily obtained in a state of purity. (Heintz.)

**Diglycol-ethylenic acid.**  $C^6H^{10}O^6 = 2 \left( \frac{C^3H^5}{H^2} O^3 \right)^n$ . (Wurtz, Compt. rend.

li. 162; Jahresb. 1859, p. 446.)—This acid is produced, together with diglycollic acid, by the oxidation of triethylenic alcohol (p. 577). This compound is oxidised by nitric acid in the same way as diethylenic alcohol; and on neutralising the resulting acid liquid with milk of lime, and proceeding nearly as described at p. 911, two calcium-salts are obtained, viz. the diglycollate, which is sparingly soluble, and the diglycolethylenate,  $C^6H^8Ca^2O^6$ , which is much more soluble, and crystallises in silky tufts, having the aspect of asbestos. The aqueous solution of this salt gives with nitrate of silver a white precipitate, from which, by decomposition with sulphuretted hydrogen and evaporation, diglycolethylenic acid may be obtained in the form of a non-crystallising syrup.

**GLYCOLLIC ETHERS.** *Oxacetic Ethers*.—By treating chloracetic acid with sodium-alcohols (methylate, ethylate, &c. of sodium), Heintz (Pogg. Ann. cix. 301 and 489; cxi. 552; cxiv. 440; Jahresb. d. Chem. 1859, p. 358; 1860, p. 314; 1861, p. 445) has obtained a number of compounds having the composition of acid glycollic ethers, that is to say, ethers derivable from glycollic acid by the substitution of a monatomic alcohol-radicle for one of the typic atoms of hydrogen, their formation being precisely analogous to that of glycollic acid itself by treating chloracetic acid with hydrate of sodium or potassium, e.g.:

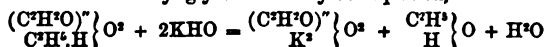


The compounds thus formed possess the essential character of the acid ethers of dibasic acids, that is to say, they are capable of exchanging one of their atoms of hydrogen, and no more, for an atom of a metal or another alcohol-radicle; ethyl-glycollic acid, for example, forms a potassium-salt,  $C^2H^3K(C^2H^3)O^2$ , and an amyl-salt,  $C^2H^3(C^4H^{11})(C^2H^3)O^2$ . But they do not appear to be acid ethers of glycollic acid in exactly the same sense that ethyl-sulphuric acid is an acid ether of sulphuric acid: for when heated with excess of alkali, they are not resolved into glycollic acid and an alcohol. Methyl-glycollic acid, for example, heated with hydrate of sodium, does not yield methylic alcohol and glycollate of sodium; neither does it yield benzo-glycollic acid when heated with benzoic acid.

The molecule of a monatomic alcohol-radicle which enters into the composition of these acid ethers appears then to be more intimately combined than in the ordinary acid ethers of dibasic acids; and for this reason Heintz supposes that this alcohol-radicle takes the place, not of an atom of typic hydrogen in the formula  $\left( \frac{C^2H^3O}{H^2} \right)^n$ , but of an atom of hydrogen within the radicle of the acid; moreover, since the ethers thus formed are monobasic acids, he derives them from a monobasic oxacetic acid represented by the formula  $\left( \frac{C^2H^3O^2}{H} \right)^n$ , and designates them as *methyl-oxacetic*,

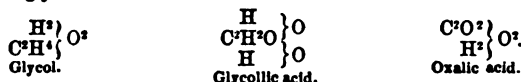
ethyl-oxacetic acid, &c. Methyl-oxacetic acid, for example, is represented by the monatomic formula  $\left\{ \begin{smallmatrix} \text{C}^2\text{H}^2(\text{CH}^3)\text{O}^2 \\ \text{H} \end{smallmatrix} \right\} \text{O}$ .

Wurtz, on the other hand (Ann. Ch. Phys. [3] lix. 161), regards these compounds as true acid ethers of glycollic acid, analogous to acid sulphate of ethyl, &c., and attributes the non-formation of glycollic acid and an alcohol, when they are heated with potash, to the fact that the neutral potassium-salt of glycollic acid ( $\text{C}^2\text{H}^2\text{K}^2\text{O}^2$ ), corresponding to the neutral glycollic ethers, does not exist, so that the decomposition represented in the case of ethyl-glycollic acid by the equation,



cannot take place. Heintz, however, has shown that when chloracetate of ethyl is heated with rather more than an equivalent quantity of glycollate of sodium, a true acid glycollate of ethyl,  $\left\{ \begin{smallmatrix} \text{C}^2\text{H}^2\text{O}^2 \\ \text{C}^2\text{H}^2\text{H} \end{smallmatrix} \right\} \text{O}^2$ , is obtained, which, when heated with excess of a metallic base, yields ethylic alcohol and a metallic glycollate. Moreover, the ethyl-salt of amyl-oxacetic acid, and the amyl-salt of ethyl-oxacetic acid, though identical in percentage composition, differ both in physical properties and chemical reactions, which could not be the case if the ethyl and amyl contained in them discharged precisely similar functions, like the two atoms of metal in an ordinary double salt.

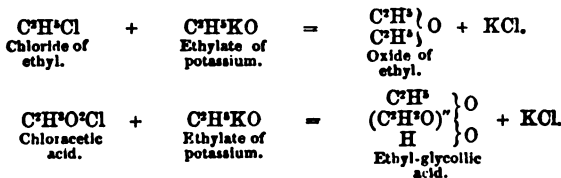
The reactions of these bodies may, however, be accounted for, without supposing them to be derived from an acid different from glycollic acid, or to be formed on any peculiar type. Glycollic acid is intermediate in composition, and therefore in properties, between glycol and oxalic acid:



Each of these compounds contains two atoms of typic, that is, replaceable hydrogen; but in glycol both these atoms are *alcoholic*, i.e. easily replaceable by acid-radicles, much less easily, and only under the influence of powerful reagents, by metals or alcohol-radicles (p. 576); and these latter, when once forced into it, are not easily displaced, e.g. by boiling with potash. In oxalic acid, on the contrary, both atoms of typic hydrogen are *saline*, that is to say, easily replaced by metals by ordinary double decomposition; while in the intermediate compound, glycollic acid, one atom of typic hydrogen is alcoholic, and the other is saline. Hence it is that glycollic acid (like its homologue, lactic acid) exhibits with metals the characters of a monobasic acid (p. 910), while, on the other hand, it easily forms derived acids in which one atom of the typic hydrogen (placed, for distinction, at the top of the formula) is replaced by an

acid radicle, e.g. *benzoylglycollic acid*,  $\left\{ \begin{smallmatrix} \text{C}^2\text{H}^2\text{O}^2 \\ (\text{C}^2\text{H}^2\text{O}^2) \\ \text{H} \end{smallmatrix} \right\} \text{O}$  (i. 548), the remaining atom of typic hydrogen (placed at the bottom) being still replaceable by metals, so that the derived acid is also monobasic. (Kekulé, *Lehrbuch*, i. 130.)

Now, when glycollic acid is formed from chloracetic acid, we may suppose that the original saline hydrogen-atom of the acetic acid retains the same functions in the glycollic acid, and that the hydrogen-atom which enters (as HO) into the place of the chlorine-atom, becomes the second (alcoholic) hydrogen-atom, replaceable by benzoyl and other acid-radicles, but not easily by metals or alcohol-radicles. The function of this hydrogen-atom is in fact almost exactly like that of the hydrogen in common alcohol. When either the one or the other is replaced by ethyl, the product does not yield alcohol by boiling with potash. Hence the following equations are not only comparable in form, but they likewise indicate similar changes of properties in the substances concerned:



We conclude, then, that ethyl-glycollic acid and its homologues (also the corresponding lactic ethers) differ from common ethers, and from isomeric compounds formed by similar replacement of the saline hydrogen (e.g. glycollate of ethyl [p. 917]) by



the action of chloracetate of ethyl on glycolate of sodium), not because they are formed on a different type, but because the alcohol-radicles are introduced into their molecules in a different manner. (On the sense in which Heintz's formulæ are admissible, see FORMULÆ, p. 704.)

**Methyl-glycollic acid.** *Methyl-oxacetic acid.*  $C^2H^3O^3 = \left( \begin{smallmatrix} CH^1 \\ C^2H^2O \\ H \end{smallmatrix} \right)^n \left\{ \begin{smallmatrix} O \\ O \end{smallmatrix} \right\}$ —Isomeric

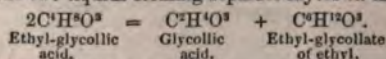
with lactic acid. Prepared by dissolving 2 at. sodium in methylic alcohol, and mixing the solution with 1 at. chloracetic acid. The mixture becomes heated and deposits chloride of sodium, and on decanting the solution of methyl-glycolate of sodium, mixing it with solution of sulphate of zinc, evaporating to dryness, and treating the residue with alcohol, a solution of methyl-glycolate of zinc is obtained. On decomposing this salt with sulphuretted hydrogen and distilling the filtrate, pure methyl-glycollic acid passes over as a colourless viscid liquid, which is nearly inodorous at ordinary temperatures, mixes with water in all proportions, and absorbs moisture from the air. Specific gravity 1.180.

**Methyl-glycolates.**—The *ammonium-salt* of this acid is a very deliquescent crystalline mass.—The *barium-salt*,  $C^2H^3BaO^3$ , forms colourless transparent prismatic crystals, easily soluble in water, nearly insoluble in alcohol.—The *calcium-salt*,  $C^2H^3CaO^3.H^2O$ , is gummy, but gives off water and becomes crystalline when left over oil of vitriol.—The *copper-salt*,  $C^2H^3CuO^3.H^2O$ , obtained by boiling the aqueous acid with carbonate of copper, forms greenish crystals soluble in water and in alcohol. The crystals are monoclinic prisms exhibiting the combination  $\alpha P, oP, [P\infty]$ . Inclination of  $\alpha P : \infty P$  in the clinodiagonal principal section =  $109^\circ - 111^\circ$ ;  $oP : \infty P = 84^\circ - 80^\circ$ .—The *lead-salt*,  $C^2H^3PbO^3$ , prepared in like manner, is soluble in water, and even in absolute alcohol, and dries up to a white crystalline mass resembling wavelite.—The *potassium-salt*,  $C^2H^3KO^3.4H^2O$ , is soluble in water and in alcohol, has a great tendency to form supersaturated solutions, and crystallises from water in large transparent prisms permanent in the air. Ether precipitates from the alcoholic solution a salt containing a smaller proportion of water, probably 3 at. (29.7 per cent.).—The *silver-salt*,  $C^2H^3AgO^3$ , is a crystalline precipitate, which separates from solution in hot water in delicate flat needles, and does not melt at  $100^\circ C$ .—The *sodium-salt*,  $C^2H^3NaO^3$ , is anhydrous, deliquescent, and is precipitated by ether from its alcoholic solution as a syrup, which dries up to a crystalline mass under the air-pump.—The *zinc-salt*,  $C^2H^3ZnO^3.H^2O$ , forms acute rhombic octahedrons truncated by the face  $oP$ , parallel to which the crystals are perfectly cleavable.  $P : P$  in the terminal edges =  $123^\circ 19'$  and  $67^\circ 23'$ ; in the lateral edges =  $146^\circ 43'$ . 100 pts. of water at  $18.4^\circ C$ . dissolve 27.4 pts. of the hydrated salt. It is also soluble in alcohol.

**Ethyl-glycollic acid.** *Ethyl-oxacetic acid.*  $C^4H^5O^3 = \left( \begin{smallmatrix} C^2H^3 \\ C^2H^2O \\ H \end{smallmatrix} \right)^n \left\{ \begin{smallmatrix} O \\ O \end{smallmatrix} \right\}$  (Heintz,

Pogg. Ann. cix. 489; cxi. 552.—Jahresb. 1859, p. 360; 1860, p. 314.)—Prepared by the action of ethylate of sodium on chloracetic acid in presence of excess of absolute alcohol. The resulting mixture is filtered from the chloride of sodium, which separates out, and the alcohol is distilled off. The residue dissolved in water is mixed with a quantity of sulphate of copper rather more than equivalent to the quantity of sodium used; the mixture is evaporated to dryness over the water-bath, and the residue is exhausted with alcohol.\* The resulting solution, which contains nothing but cupric ethyl-glycolate, together with cupric chloride, is evaporated, and the residue repeatedly crystallised from water. To prepare the acid, the copper-salt is decomposed in hot aqueous solution by sulphydric acid, and the clear liquid is distilled, the portion which goes over at about  $200^\circ C$ . being collected apart.

At a higher temperature the acid is decomposed, yielding a colourless distillate, which after a while deposits white pulverulent dioxymethylene,  $C^2H^4O^2$  (see METHYLENE); but if the distillation be so conducted that the undecomposed acid can flow back again, it is for the most part resolved into glycollic acid, which remains in the retort, and ethyl-glycolate of ethyl,  $C^2H^2(C^2H^3)(C^2H^3)O^3$ , which distils over together with aqueous ethyl-glycollic acid, the two liquids forming separate layers in the receiver:



Ethyl-glycollic acid distilled with iodide of phosphorus gives off iodide of ethyl and acetic acid, and leaves a residue containing glycollic acid.

**Ethyl-glycolates.**—The *barium-salt*,  $C^4H^5BaO^3$ , is very soluble in water and in alcohol, and crystallises after some time from the syrupy solution.

\* The undissolved residue contains, besides sulphate of copper, a small quantity of a copper-salt, sparingly soluble in water, and having the composition of glycolate of copper,  $C^2H^3CuO^3$ .



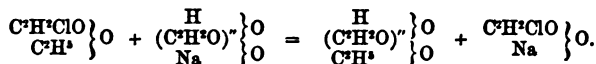
The *copper-salt*,  $C^2H^3CuO^2.H^2O$ , crystallises in oblique rhombic prisms of a fine blue colour, which melt and give off their crystallisation-water when heated. 100 pts. water at  $14^\circ C$ . dissolve 12.34 pts. of the anhydrous, and 14.22 pts. of the crystallised salt; 100 pts. of alcohol of specific gravity 0.826 dissolve 1.74 pts. of the hydrated salt at  $13.5^\circ C$ .—The *silver* and *mercurous* salts are white precipitates formed in concentrated solutions and partially reduced at the boiling heat.—The *zinc-salt* is not crystallisable.

*Ethyl-glycollate of Ethyl*,  $C^2H^{12}O^3 = \left. \begin{matrix} C^2H^3 \\ (C^2H^2O)^n \\ C^2H^3 \end{matrix} \right\} O$ , is obtained as already described by the decomposition of ethyl-glycollic acid. Its properties have not been examined.

*Ethyl-glycollate of Amyl*,  $C^2H^{18}O^3 = \left. \begin{matrix} C^2H^3 \\ (C^2H^2O)^n \\ C^2H^{11} \end{matrix} \right\} O$ , obtained by digesting a mixture of ethyl-glycollate of sodium and iodide of amyl diluted with absolute alcohol, in a sealed tube, decanting the resulting liquid from the iodide of sodium which separates, treating it with mercury to remove excess of iodine, and rectifying,—is a transparent, colourless, rather viscid liquid, sinking slowly in water, of agreeable fruity odour, boiling between  $180^\circ$  and  $190^\circ C$ ., soluble in all proportions in alcohol and ether. It is decomposed by alcoholic potash, emitting the penetrating odour of amyl alcohol. (O. Siemens.)

**Glycollate of Ethyl.**  $C^2H^4O^3 = \left. \begin{matrix} H \\ (C^2H^2O)^n \\ C^2H^3 \end{matrix} \right\} O$  (Heintz, Jahresb. 1861, p. 446.)

—This compound, isomeric, but not identical with ethyl-glycollic acid, is produced by heating chloracetate of ethyl with rather more than an equivalent quantity of glycollate of sodium to  $130^\circ$ — $150^\circ C$ .:



It dissolves in water, forming a solution which does not exhibit an acid reaction. By boiling with alkalis, it is decomposed, yielding ethylic alcohol and an alkaline glycollate, a reaction by which it is distinguished from the preceding compound. With aqueous ammonia it forms glycollamide (p. 908).

*Acetoglycollate of Ethyl*,  $C^2H^{10}O^4 = \left. \begin{matrix} C^2H^3O \\ (C^2H^2O)^n \\ C^2H^3 \end{matrix} \right\} O$ .—Produced by heating chloracetate of ethyl with acetate of sodium. It is an oily, mobile liquid, of specific gravity 1.0093 at  $17^\circ C$ ., boiling at  $179^\circ$ . With alcoholic ammonia, it yields glycollamide and acetamide, together with glycollate and acetate of ammonium. With a small quantity of ammonia, the products are glycollamide and acetate of ethyl. Aqueous bases decompose it, for the most part, forming acetates and glycollates; but by mixing it with water, and somewhat less than an equivalent quantity of slaked lime, it may be converted into *acetoglycollate of calcium*,  $C^2H^8CaO^4$ . (Heintz, Ann. Ch. Pharm. cxxiii. 325.)

**Amyl-glycollic acid.** *Amyl-oxacetic acid.*  $C^2H^{14}O^3 = \left. \begin{matrix} C^2H^{11} \\ (C^2H^2O)^n \\ H \end{matrix} \right\} O$  (Heintz, Pogg. Ann. cix. 301; Jahresb. 1859, p. 358.—O. Siemens, *Inaugural Dissertation*, Göttingen, 1861; Jahresb. 1861, p. 449.)—Produced by the action of amylate of sodium on chloracetic acid. To obtain it in the pure state, 98.6 grms. of sodium are dissolved in amyl alcohol, and to the resulting amylate of sodium, kept in the liquid state by heat, is added a solution of 190 grms. chloracetic acid in amyl alcohol: the liquid, filtered from chloride of sodium, is freed from excess of amyl alcohol partly by distillation, partly by agitation with water. The aqueous solution of amyl-glycollate of sodium thus obtained is decomposed by excess of hydrochloric acid; the amyl-glycollic acid which rises to the surface is removed, and the portions of acid still remaining in the watery liquid are dissolved out by agitation with ether. The whole of the amyl-glycollic acid thus obtained is then subjected to fractional distillation till a distillate is obtained boiling at about  $135^\circ C$ . (Siemens.)

Amyl-glycollic acid is a not very mobile liquid, of specific gravity 1.003, boiling at  $235^\circ C$ ., sparingly soluble in water, but soluble in all proportions in alcohol and ether. It burns with a bright smoky flame, giving off a pungent odour.

*Amyl-glycollates.*—The *barium-salt* is not crystallisable (Heintz).—The *copper-salt*,  $C^2H^{12}CuO^3$ , obtained by recrystallising the precipitate formed on mixing the solutions of equivalent quantities of amyl-glycollate of sodium and sulphate of copper, forms small blue-green crystals, appearing under the microscope as right

prisms with truncated end-faces. It is moderately soluble in alcohol, very slightly in water and in ether. It melts at  $110^{\circ}$  C. to a green liquid, and gradually decomposes (Siemens).—The *mercurous salt*\*,  $\text{C}^{\text{H}}^{\text{H}}\text{HgO}^{\text{H}}$ , is obtained by precipitation as a white powder, which melts with decomposition at  $170^{\circ}$  C., is very sparingly soluble in water, more soluble in alcohol, insoluble in ether.—The *potassium-salt*,  $\text{C}^{\text{H}}^{\text{H}}\text{KO}^{\text{H}} \cdot \text{H}^{\text{O}}$ , is obtained by neutralising the acid with alcoholic potash, removing the excess of potash by carbonic acid, filtering, evaporating, and crystallising from a small quantity of alcohol. It crystallises with difficulty in long oblique rhombic prisms with terminal faces very much inclined to the principal axis. At  $10^{\circ}$  to  $15^{\circ}$  C. it crystallises in thin, nearly rectangular plates, resembling the sodium-salt. It is very soluble in water and in alcohol, and is precipitated from the alcoholic solution by ether in the crystalline form. It gives off its water without melting at  $120^{\circ}$  C., and melts, without decomposition, between  $200^{\circ}$  and  $210^{\circ}$  C. It deliquesces slowly when exposed to the air.—The *silver-salt*,  $\text{C}^{\text{H}}^{\text{H}}\text{AgO}^{\text{H}}$ , is obtained, by double decomposition, as a white curdy precipitate, soon becoming light red, and, after being washed and dissolved in a large quantity of boiling water, separates, on cooling, in slender rose-red needles. It dissolves with moderate facility in alcohol, sparingly in water, not at all in ether. When perfectly pure it is white, but decomposes quickly in contact with the air; at  $110^{\circ}$  C. it melts and decomposes.—The *sodium-salt*,  $\text{C}^{\text{H}}^{\text{H}}\text{NaO}^{\text{H}} + 2\text{H}^{\text{O}}$ , crystallises from alcohol in thin, colourless, rectangular plates, which dissolve readily in water and in alcohol, are insoluble in ether, give off their water of crystallisation without deliquescing, and melt without decomposition, between  $190^{\circ}$  and  $200^{\circ}$  C. When exposed to the air they effloresce, after a while, without deliquescing. (Siemens.)

*Amyl-glycollate of ethyl.*  $\text{C}^{\text{H}}^{\text{H}}\text{O}^{\text{H}} = \frac{\text{C}^{\text{H}}^{\text{H}}}{\text{C}^{\text{H}}^{\text{H}}} \left\{ \begin{matrix} \text{O} \\ \text{O} \end{matrix} \right\}$ .—Prepared by digesting a mixture of amyl-glycollate of sodium and iodide of ethyl diluted with absolute

alcohol, in a sealed tube, at the heat of the water-bath, for four days; decanting the liquid from the iodide of sodium produced in the reaction; shaking it up with mercury to remove free iodine; subjecting it to fractional distillation; treating the distillate, obtained between  $205^{\circ}$  and  $210^{\circ}$  C., with carbonate of sodium, to remove free amyl-glycollic acid; dehydrating the neutral ether thus obtained; rectifying it, and collecting the portion which passes over at  $212^{\circ}$  C. It is a colourless, mobile liquid, having an ethereal odour. When decomposed by alcoholic potash, it does not emit the odour of amylic alcohol, by which character, as well as by its higher boiling point, it is distinguished from the isomeric compound ethyl-glycollate of amyl (p. 917).

*Phenyl-glycollic acid.* *Phenyl-oxacetic acid.*  $\text{C}^{\text{H}}\text{O}^{\text{H}} = \frac{\text{C}^{\text{H}}^{\text{H}}}{\text{H}} \left\{ \begin{matrix} \text{O} \\ \text{O} \end{matrix} \right\}$ .—When

a mixture of phenylate of sodium and chloracetic acid is heated for a considerable time and then left to cool, phenyl-glycollate of sodium is obtained as a gradually solidifying mass; and by decomposing the aqueous solution of this salt with hydrochloric acid, impure phenyl-glycollic acid is obtained as a brown oily liquid, which, by repeated solution in lukewarm water and evaporation, yields very thin silky needles, melting in warm water to a heavy oil. These crystals yielded by analysis numbers intermediate between  $\text{C}^{\text{H}}\text{O}^{\text{H}}$  (phenyl-glycollic acid) and  $\text{C}^{\text{H}}^{\text{H}}\text{O}^{\text{H}}$  (cresyl-glycollic acid).

*Phenyl-glycollate of barium*,  $\text{C}^{\text{H}}\text{BaO}^{\text{H}} \cdot \frac{3}{2}\text{H}^{\text{O}}$ , forms large, thin, very brittle laminae. The *copper-salt*,  $\text{C}^{\text{H}}\text{CuO}^{\text{H}} \cdot \text{H}^{\text{O}}$ , forms sparingly soluble, microscopic, prismatic or tabular crystals.—The *sodium-salt*,  $\text{C}^{\text{H}}\text{NaO}^{\text{H}} \cdot \frac{1}{2}\text{H}^{\text{O}}$ , crystallises from absolute alcohol in extremely slender needles.—The aqueous solution of this salt forms with nitrate of silver a sparingly soluble precipitate, which, when crystallised from hot water, yields the *silver-salt*,  $\text{C}^{\text{H}}\text{AgO}^{\text{H}}$ , in slender concentrically grouped needles.—The aqueous solution of the sodium-salt also yields precipitates with acetate of lead and mercurous nitrate.

When the warm concentrated aqueous solution of a phenyl-glycollate is mixed with hydrochloric acid, phenyl-glycollic acid separates from it as an oil; the cold solution heated with hydrochloric acid first becomes milky, and then on agitation yields crystalline flakes, which are easily fusible and likewise sublimed when heated for some time in the water-bath. 100 pts. of water dissolve rather more than 1 pt. of the acid; it is easily soluble in alcohol and ether. (Heintz.)

*Cresyl-glycollic Acid.* *Cresyl-oxacetic acid.*  $\text{C}^{\text{H}}^{\text{H}}\text{O}^{\text{H}} = \frac{\text{C}^{\text{H}}^{\text{H}}}{\text{H}} \left\{ \begin{matrix} \text{O} \\ \text{O} \end{matrix} \right\}$ .—The mother-liquor of the impure phenyl-glycollate of sodium, obtained as above described

\* Hg = 200.

(p. 918), yielded another sodium-salt, easily soluble in alcohol, difficult to crystallise, and separated by ether from the alcoholic solution, not in needles like the phenyl-glycollate, but as a gelatinous mass. From this salt the acid was separated by hydrochloric acid, and the solution of the ammonium-salt, and a sparingly soluble copper-salt,  $C^6H^5CuO^2 \cdot H^2O$ , were prepared. (Heintz.)

**GLYCOLLIDE.**  $C^6H^5O^2$ . *Glycollic anhydride*.—A compound isomeric with glyoxal, and differing from glycollic acid by 1 at. water. It is produced:—1. By heating glycollic acid to  $200^\circ$ — $240^\circ$  C., small quantities of diglycollic acid and dioxymethylene being formed at the same time. (Heintz, Pogg. Ann. cxv. 452; Jahresb. 1861, p. 444.)

2. By the action of heat on chloracetate of potassium:



If the crystallised chloracetate is used, the greater part of the glycollide thus produced unites with water contained in the salt, and is converted into glycollic acid. (Kekulé, Ann. Ch. Pharm. cxv. 288.)

3. By boiling chloracetic acid with water, and evaporating the acid liquid, which also contains hydrochloric acid, to dryness, a residue is obtained, containing glycollide. (Heintz, loc. cit.)

4. By heating tartaric acid to  $180^\circ$  C., as long as carbonic anhydride continues to escape, pulverising the residual mass as soon as it has become solid, which takes several days, and washing it with hot water:



It was by this process that glycollide was first obtained. (Dessaigues, Compt. rend. xxxviii. 46.)

Glycollide is a white tasteless substance, insoluble in cold and very slightly soluble in hot water. It melts at  $180^\circ$  C. without loss of weight. It dissolves in potash, yielding glycollate of potassium. Heated with ammonia, it forms glycollamide (p. 909).

**GLYCOLS.** *Diatomic Alcohols*.—Bodies formed on the general type:



$n = 2$  giving the ethylenic,  $n = 5$  the amylene glycols, &c. The glycols of each series are di- or polyatomic, according as  $p$  is equal to or greater than unity. The general properties of these compounds are described under the articles ALCOHOLS (i. 102) and ETHERS (ii. 517, 522). The glycols of amylene (i. 208; ii. 9), ethylene (ii. 574), tetraylene, or butylene, and tritylene, or propylene, have been obtained; but the ethylenic compounds and their derivatives are the only ones that have been very completely studied.

**GLYCOSINE.**  $C^6H^5N^1 = N^1(C^6H^5)^2$ . (Debus, Ann. Ch. Pharm. cvii. 199.)—An organic base produced by the action of ammonia on glyoxal:



When a syrupy solution of glyoxal, heated to  $60^\circ$  or  $70^\circ$  C., is mixed with three times its volume of strong aqueous ammonia at the same temperature, the liquid turns brown, effervesces slightly, and after a while deposits small crystalline needles. When the quantity of these crystals no longer increases at the temperature above-mentioned, the liquid is left to cool; the still strongly-coloured crystals are separated by filtration, washed with cold water, and dissolved in very dilute hydrochloric acid; the solution is decolorised by animal charcoal; and the filtrate is slowly mixed with very dilute ammonia; it then deposits glycosine as a crystalline powder; if it is not colourless, the solution in hydrochloric acid, &c. must be repeated.

Glycosine is a pulverulent substance, consisting of truncated striated prisms, becoming strongly electric by trituration, soft to the touch, tasteless and inodorous. When heated on platinum-foil, it volatilises without melting and leaves no residue; it may be sublimed by careful heating between two watch-glasses, and then forms a bulky sublimate consisting of needle-shaped crystals. It is nearly insoluble in cold, sparingly soluble in boiling water; easily in hydrochloric and acetic acids. The hydrochloric acid solution concentrated over the water-bath yields large crystals of *hydrochlorate of glycosine*; with oxalate of ammonium it forms, especially on stirring, a crystalline precipitate of *oxalate of glycosine*; with iodide of potassium, no precipitate; with cupric chloride, a green; with mercuric chloride, a heavy crystalline precipitate.

**GLYCYRRETIN.**  $C^6H^{10}O^4$ ? (Gorup-Besane, Ann. Ch. Pharm. cxviii. 236.)—A substance obtained, together with glucose, by heating dilute acids.



It is a brownish-yellow brittle resin, which does not m insoluble in water, but soluble in alcohol and in alkalis. phuric acid, forming an amaranth-red solution, the colour to purple-violet, and becomes violet on dilution with w being at the same time precipitated. The alcoholic sol animal charcoal. No satisfactory analysis has yet been n

**GLYCYRRHIZIN.**  $C^{24}H^{36}O^9$ . (A. Vogel, Jun., J Ann. Ch. Pharm. lix. 224.—Gorup-Besanez, *ibid.* cxvi stance contained in the root of liquorice (*Glycyrrhiza glabr prepared from Russian liquorice-root (which yields a less col product than the Spanish root), by precipitating the filte infusion with dilute sulphuric acid; washing the dark till it is quite free from sulphuric acid; then dissolving i 82 per cent., and mixing the not too concentrated solut ether as long as a dark-coloured resinous substance is th on evaporation leaves glycyrrhizin, as an amorphous sul containing but a very small quantity (0.2 per cent.) Vogel and Lade adopted a similar process, but evaporate out first freeing it from the dark resinous substance by (Jahresb. 1860, p. 551) precipitates the aqueous extract o of potassium (cream of tartar), digests the precipitate i alcoholic filtrate to dryness.*

Glycyrrhizin is a light yellow amorphous substance, ha soluble in cold, easily soluble in hot water, soluble also and in ether by the aid of a gentle heat; alkalis dis colour; the solutions yield with acids a precipitate part acid. The aqueous solution is precipitated by chloride nesium, sulphate of copper, chloride of copper, and basic

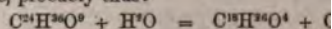
The constitution of glycyrrhizin is determined by the

	Calculation.		Vogel
$C^{24}$	288	61.5	61.
$H^{36}$	36	7.6	7.
$O^9$	144	30.9	30.
$C^{24}H^{36}O^9$	468	100.0	100.

The analytical numbers might of course be equally wel formula  $C^{24}H^{36}O^9$ ; but the calcium-salt of glycyrrhizin c Besanez, 53.9 per cent. C, 7.1 H, 30.77 O, and 8.29  $Ca^{20}$   $2C^{24}H^{36}O^9 \cdot 3Ca^{20}O_4H^{10}$ , and the lead-salt  $24.0 C$ , 2.9 H, 1 agreeing with  $C^{24}H^{36}O^9 \cdot Pb^{20}O_4PbH^2O$ . Hence the formu be  $C^{24}H^{36}O^9$ . Lade obtained, by the analysis of glycyrr and 7.1 to 7.4 H; but his glycyrrhizin was impure, contai

Glycyrrhizin is not fermentable. Nitric acid acts upo off abundant red fumes, and forming a light yellow subs action becomes stronger, and a pale yellow crystallisable oxypicric acid, together with oxalic acid. It is also vio of chromate of potassium, or peroxide of manganese, an Besanez.)

By boiling with dilute sulphuric and other acids, glycyrretin and glucose, probably thus:



**GLYOXAL.**  $C^2H^2O^2 = (C^2O^2)^2 \cdot H^2$ . (Debus, Ann. ex. 316; cxviii. 253.—Gm. xii. 503.)—This compound ma of glyoxylic and of oxalic acid, and stands between ethyl lene) and oxalic acid, in the same manner as common alde (hydrate of ethyl) and acetic acid.

$C^2H^2O$	— $H^2$	=	$C^2H^4O$	=	Aldehyde.
Alcohol.					
$C^2H^2O^2$	— $H^4$	=	$C^2H^2O^2$	=	Glyoxal.
Glycol.					

It is produced, together with glyoxylic acid and othe nitric acid upon alcohol. When the syrupy neutral liqui of glyoxylic acid, is mixed with several times its volume and the mixture is left to itself for some hours, the sides

with a white crystalline crust, consisting of a compound of glyoxal with the acid sulphite; and by dissolving this compound in the smallest possible quantity of boiling water, and leaving the filtrate to cool quietly, the compound is obtained in fine crystals, which may be purified by two recrystallisations. A further quantity may be obtained by treating the mother-liquors with alcohol. The sodium-compound, mixed with chloride of barium, yields, after two days, crystals of the corresponding barium-compound; and, by exactly decomposing the barium-compound with sulphuric acid, and evaporating the filtrate to remove water and sulphurous acid, glyoxal is obtained in the solid state.

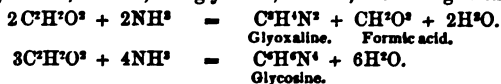
Glyoxal appears, also, to occur among the products of the oxidation of ethylenic glycol by nitric acid; but its presence has not been distinctly proved.

Glyoxal is a transparent, slightly yellowish, amorphous mass, which deliquesces readily when exposed to the air, and dissolves with great facility in water, alcohol, and ether. The aqueous solution is merely clouded by *neutral acetate of lead*; but, on adding ammonia, a copious white precipitate is produced. With *nitrate of silver* and *ammonia* it forms a beautiful speculum of silver. A small quantity of very dilute *nitric acid* converts glyoxal into glyoxylic acid; by a larger quantity, even of very dilute nitric acid, it is converted into oxalic acid.

*Caustic fixed alkalis* convert it into a salt of glycollic acid, *e. g.*:



A syrupy solution of glyoxal, gently heated with strong aqueous *ammonia*, yields two bases—viz., glyoxaline,  $\text{C}^2\text{H}^2\text{N}^2$ , and glycosine,  $\text{C}^2\text{H}^2\text{N}^2$ ,\* according to the equations—



Glyoxaline is by far the more abundant product of the two.—Glyoxal is decomposed by *sulphydic acid*.

*Compounds of Glyoxal*.—When a stream of *ammonia-gas* is passed into an ethereal solution of glyoxal, a white precipitate is formed, consisting of glyoxal-ammonia.

Glyoxal, like other aldehydes, forms crystalline compounds with the *acid sulphites of alkali-metals*. The *ammonium-salt*,  $\text{C}^2\text{H}^2\text{O}^2 \cdot 2(\text{NH}^2)\text{HSO}^2$  forms shining prismatic crystals, very soluble in water, insoluble in alcohol. The aqueous solution is precipitated by acetate of lead, but not by salts of zinc, copper, or silver.

The *barium-salt* is deposited from the hot saturated solution in concentrically-grouped masses, containing  $\text{C}^2\text{H}^2\text{O}^2 \cdot 2(\text{BaHSO}^2) \cdot \frac{1}{2}\text{H}^2\text{O}$ . The aqueous solution of this salt, boiled with a slight excess of caustic baryta, yields a precipitate of neutral sulphite of barium, while free baryta and glycollate of barium remain in solution:



The *sodium-salt*,  $\text{C}^2\text{H}^2\text{O}^2 \cdot 2(\text{NaHSO}^2) \cdot \text{H}^2\text{O}$ , forms small hard crystals, easily soluble in water, insoluble in alcohol. The aqueous solution, after boiling for some time, precipitates acetate of lead and chloride of barium.

**GLYOXALINE.**  $\text{C}^2\text{H}^2\text{N}^2$ . (Debus, Ann. Ch. Pharm. cvii. 199.)—An organic base produced simultaneously with glycosine by the action of strong aqueous ammonia on glyoxal. When the brown mother-liquor from which the glycosine has separated, is evaporated to a syrup at a gentle heat to expel free ammonia, a syrupy uncrystallisable residue is left, which, when mixed with twice its volume of a saturated solution of oxalic acid, soon deposits a large quantity of crystals of oxalate of glyoxaline (the mother-liquor retaining formic acid, *vid. sup.*), which may be purified by solution in water, treatment with animal charcoal, and recrystallisation. From this salt the base may be separated by mixing the solution with chalk, heating it for some time to  $100^\circ \text{C}$ ., and evaporating the filtered liquid.

Glyoxaline crystallises with difficulty, and only from a syrupy solution, in concentrically grouped crystals. It melts easily; has a faint fishy odour; volatilises at a higher temperature in thick white vapours; deliquesces in damp air; dissolves easily in water, forming a solution which turns turmeric brown and reddened litmus blue; neutralises strong acids; precipitates the chlorides of iron and copper (the latter precipitate re-dissolving with blue colour in excess of glyoxaline), and nitrate of silver, but not calcium-salts.

*Chloroplatinate of glyoxaline*,  $\text{C}^2\text{H}^2\text{N}^2 \cdot \text{HClPtCl}_2$ , is a yellow crystalline precipitate, which dissolves in hot water, and separates in orange-red prisms.

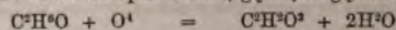
The *oxalate*,  $\text{C}^2\text{H}^2\text{N}^2 \cdot \text{C}^2\text{H}^2\text{O}^2$ , forms colourless prisms, which do not undergo any

\* Kekulé (*Lehrb. II. 23*) suggests that glyoxaline and glycosine may possibly be isomeric, and related to one another in the same manner as hydrobenzamide and asarine.

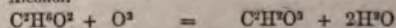
alteration at 125° C., but when heated on platinum-foil, melt easily and volatilise in white fumes.

**GLYOXYLIC ACID.**  $C^2H^2O^3$ . Syn. *Glyoxalic acid*. (Kekulé, p. 923, footnote. Debus, Phil. Mag. [4] xii. 361; Ann. Ch. Pharm. e. 1; cii. 28; ex. 316.—Gm. xii. 505; xiii. 434.)—This acid is produced, together with glycollic acid and other compounds:

1. By the action of nitric acid upon alcohol, glycol, or glyoxal (Debus):



Alcohol.

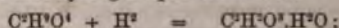


Glycol.



Glyoxal.

2. By the action of nascent hydrogen upon oxalic acid:



*e. g.* when oxalate of sodium is submitted to the action of sodium-amalgam in presence of water; or oxalate of zinc to that of zinc and dilute sulphuric acid. When the action is not accelerated by elevation of temperature, and a large quantity of salt is used, glyoxylic acid is the chief product; in the contrary case, glycollic acid. (Church, Chem. Soc. J. [2] i. 301.)

*Preparation.*—1. *From Alcohol.*—220 grms. of alcohol of 80 per cent. are poured into a tall narrow flask capable of holding about 1½ lb. of water; 100 grammes of water are introduced below the alcohol by means of a funnel having its neck finely drawn out; and below this are poured 200 grms. of red fuming nitric acid, so that the three liquids may remain one above the other and mix as little as possible at first. The bottle is then closed with a cork fitted with a gas-delivery tube dipping under water, and the whole is left for six or eight days, at a temperature of 20° to 22° C., till the liquids have become completely mixed, and the resulting nitrite of ethyl has volatilised. The residual liquid—containing nitric, acetic and formic acids, compound ethers, glyoxal and other aldehydes, glycollic acid and glyoxylic acid—is evaporated to a syrup over the water-bath in portions of 20 to 30 grms. each; the residues, containing oxalic, glycollic and glyoxylic acids, together with the less volatile aldehydes, are dissolved in small quantities of water; the united solutions are neutralised with chalk; the neutral liquid is mixed with an equal volume of alcohol; and the resulting precipitate of calcium-salts pressed and repeatedly boiled with water. The aqueous extract yields crystals of glyoxylate of calcium, and a further quantity of this salt may be obtained by concentrating the mother-liquor. The subsequent mother-liquors yield a double salt of glycolate and glyoxylate of calcium, and the last contain glycolate of calcium (p. 911).

2. *From Oxalic acid.*—A large quantity of oxalate of zinc is placed, together with a few pieces of pure zinc, in a beaker, the mixture covered with water, and dilute sulphuric acid added slowly drop by drop. Milk of lime is then added in slight excess, together with a large quantity of water; the mixture is warmed, filtered, supersaturated with carbonic acid, and again warmed and filtered; the filtrate thus obtained deposits on cooling needle-shaped crystals of glyoxylate of calcium. Or better: the mixture of zinc-salts is shaken up with ether, the syrupy ethereal extract thus obtained is treated with carbonate of calcium, and the various calcium-salts thus obtained are separated by Debus's method. (Church.)

The hydrated acid is obtained by decomposing the calcium-salt with oxalic acid, and evaporating the solution in vacuo, in the form of a viscid, transparent, slightly yellowish syrup, which dissolves readily in water. The solution heated to 100° C., gives off unaltered glyoxylic acid, together with the watery vapours. The syrupy acid, when strongly heated, gives off acid vapours and volatilises, leaving a scanty black residue. (Debus.)

A solution of glyoxylic acid treated with *sulphydric acid* yields nodular crystals apparently containing a sulphuretted acid. A strong solution of glyoxylate of calcium repeatedly treated with *sulphydric acid* yields the salt  $C^2H^2Ca^2 \left\{ \begin{smallmatrix} O^3 \\ S \end{smallmatrix} \right. . 3H^2O$ , the acid of which consists of a double molecule of glyoxylic acid, having one-fifth of its oxygen replaced by sulphur. (Debus.)

Glyoxylic acid dissolves *zinc*, without evolving an equivalent quantity of hydrogen, the hydrogen in fact uniting with the glyoxylic acid to form glycollic acid. (Debus.)

The *glyoxylates*,  $C^2HMO^3$ , are obtained by neutralising the bases or their carbonates with the aqueous acid. Most of them contain 1 at. of water, of which they cannot be deprived without undergoing further decomposition. For this reason, Debus at



first assigned to them the formula  $C^2H^2MO^4$ , regarding the acid as  $C^2H^2O^4$ . But the composition of the ammonium-salt shows that the true formula of the acid is  $C^2H^2O^3$ , which is likewise more in accordance with its general relations.\*

It is not exactly known whether glyoxylic acid is capable of forming salts with 2 at. metal. An insoluble lead-salt,  $C^2Pb^2O^3.H^2O$  is produced by double decomposition, but it is perhaps a basic salt,  $C^2HPbO^3.PbHO$ . From the solution of the calcium-salt  $C^2H^2CaO^3.H^2O$ , lime-water throws down a white precipitate, which is perhaps the neutral calcium-salt  $C^2Ca^2O^3$ ; but on the other hand it is possible that the original calcium-salt may simply be rendered insoluble by the addition of the lime-water. (Kekulé.)

The glyoxylates unite with sulphites. A strong solution of acid sulphite of sodium mixed with syrupy glyoxylic acid yields the double salt  $C^2HNaO^3.NaHSO^3$ ; and by passing sulphurous acid gas into water in which glyoxylate of calcium is suspended, and concentrating the resulting solution, crystals of the salt  $2C^2H^2CaO^3.CaHSO^3.5H^2O$  are obtained. (Debus.)

*Glyoxylate of Ammonium*,  $C^2H(NH^4)O^3$ , prepared by precipitating the calcium-salt with oxalate of ammonium, and evaporating in vacuo over sulphuric acid, forms small prismatic crystals, easily soluble in water. The concentrated solution turns yellow when boiled, or when evaporated at  $100^\circ C$ . It forms crystalline precipitates with nitrate of silver and acetate of lead, also with sulphate of copper after a while. Potash evolves ammonia from it even at ordinary temperatures. It gives by analysis 26.70 per cent. C, and 5.75 H (by calculation 26.4 C and 5.5 H).

*Glyoxylate of Barium*,  $C^2HBaO^3.2H^2O$ .—Prepared by digesting diluted glyoxylic acid at ordinary temperatures with carbonate of barium till the acid is completely neutralised, and evaporating the filtrate in vacuo. At a certain degree of concentration, the salt begins to separate in small white crystals. It is partly resolved into glycollic acid and oxalate of barium when heated to  $120^\circ C$ , or when its aqueous solution is raised to the boiling point. With lime-water, acetate of lead, and nitrate of silver, it behaves like the calcium-salt. By analysis it gives 39.4 per cent. barium, the above formula requiring 38.9 per cent.

*Glyoxylate of Calcium*,  $C^2H^2CaO^3.H^2O$ , crystallises in thin needles or hard prismatic crystals, soluble in 177 parts of water at  $8^\circ C$ , and yielding by analysis 18.2 per cent. calcium (calculation 18.01). It may be heated to between  $160^\circ$  and  $170^\circ C$ . without loss of weight, but at  $180^\circ$  it gives off water and carbonic anhydride, and yields glycollic acid and carbonate of calcium, together with a resinous substance. Lime-water added to the solution of this salt immediately produces a copious precipitate, which, immediately after its formation, dissolves readily in acetic acid, but if left to itself for awhile, or more quickly if boiled for a few seconds with the liquid, becomes insoluble in acetic acid, being in fact resolved into glycollic acid and oxalate of calcium:



This reaction affords the means of separating glyoxylic from glycollic acid, when the two occur together, a solution of pure glycollic acid of calcium not being precipitated by lime-water. It also serves for the quantitative estimation of glyoxylic acid, 128 pts. (1 at.) of oxalate of calcium ( $C^2Ca^2O^4$ ) corresponding to 198 pts. (2 at.) of the glyoxylate ( $C^2H^2CaO^3.H^2O$ ).

Glyoxylate of calcium forms double salts with *glycollic* and *lactic* acid of calcium. (See page 911, and LACTIC ACID.)

An *ammonioglyoxylate of calcium*,  $3C^2H^2CaO^3.2NH^3.H^2O$ , is obtained in crystals on pouring chloride of calcium into a solution of glyoxylate of ammonium in the smallest possible quantity of water. The same salt is obtained in the anhydrous state by adding ammonia to a boiling saturated solution of glyoxylate of calcium.

*Glyoxylate of Lead* forms with ammonia a compound containing 7 at.  $C^2HPbO^3$  to  $4NH^3$ .

*Glyoxylate of Potassium* is deliquescent and difficult to crystallise.

*Glyoxylate of Silver*,  $C^2HAgO^3.H^2O$ , is obtained as a white crystalline powder, by precipitating nitrate of silver with glyoxylate of ammonium. It is but sparingly soluble in cold water, and is rapidly decomposed by light. Analysis gave 54.1 and 53.9 per cent. silver, the formula requiring 54.2 per cent. It unites with ammonia, forming a salt containing 4 at.  $C^2HAgO^3$  to  $3NH^3$ . (Debus.)

*Glyoxylate of Zinc*,  $C^2HZnO^3.2H^2O$ .—Produced as a white crystalline precipitate on adding a strong solution of glyoxylate of calcium to acetate of zinc. It dissolves sparingly in water, easily in acetic acid, hydrochloric acid, and caustic potash. After drying over oil of vitriol, it gave by analysis 38.09 and 38.73 per cent. zinc, the

\* Kekulé (Zehrs H. 20) applies the term glyoxallic acid to the compound  $C^2H^2O^3$ , and glyoxylic acid to the acid  $C^2H^2O^4$ , produced by the decomposition of bromoglycolate of silver (p. 913), and by the reduction of oxalic acid.

formula requiring 37·64 per cent. The 2 at. water cannot be removed without decomposing the salt.

**GMELINITE.** *Soda Chabasite. Hydrolite. Herschelite.*—A hydrated silicate aluminium, calcium, and sodium, whose composition is expressed by the same general formula as that of chabasite, viz.,  $M^2O \cdot Al^2O^3 \cdot 4SiO^2 \cdot 6H^2O$ , or  $(M^{2P})Si^2O^4 \cdot 3H^2O$ , but with a larger proportion of sodium. It occurs crystallised in hexagonal pyramid having the terminal summits and lateral edges truncated (P. oP.  $\infty$ P). Angle P:P the terminal edges =  $142^\circ 26'$ ; in the lateral edges,  $80^\circ 8'$ ; oP:P =  $139^\circ 56'$ . It is usually, however, regarded as rhombohedral, and the crystals as twins secondary to rhombohedron of  $86^\circ 18'$ . It is distinguished from chabasite by its perfect cleavage parallel to the faces of a six-sided prism (G. Rose). Hardness = 4·5; specific gravity = 2·04–2·12; lustre vitreous; colourless, yellowish-white, reddish-white, or flesh-red translucent; brittle. It behaves like chabasite before the blow-pipe, and gelatinises with hydrochloric acid.

The following are analyses of gmelinite from Glenarm:—*a.* By Connell (Edinburgh Phil. J. 1838). *b* and *c* by Rammelsberg (Pogg. Ann. xlix. 211):

SiO <sup>2</sup>	Al <sup>2</sup> O <sup>3</sup>	Fe <sup>2</sup> O <sup>3</sup>	Ca <sup>2</sup> O	Na <sup>2</sup> O	K <sup>2</sup> O	H <sup>2</sup> O	
48·56	18·05	0·11	5·13	3·85	0·39	21·66	= 97·75
46·40	21·09	...	3·67	7·29	1·60	20·41	= 100·46
46·56	20·18	...	3·89	7·09	1·87	20·41	= 100·00

Gmelinite occurs in amygdaloid rocks at Montecchio Maggiore, and at Castel in the Vicentine, at Glenarm, county of Antrim, Ireland, and in the island Magee.

*Herschelite* from Etna has the same formula as gmelinite, but with  $\frac{1}{2}$  less water.

*Ledrerite*, from Jackson, Nova Scotia, has the form of gmelinite, and likewise the same composition, but with only one-third the amount of water. (Dana, ii. 321.)

**GNAPHALIUM.** The ash of *Gnaphalium leontopodium*, L., has been examined by A. Bauer (Wien, Akad. Ber. xxxvi. 200). 100 pts. of the plant (stem, leaves, and flowers) yielded 6·5 pts. ash, containing, after deduction of charcoal and sand:

K <sup>2</sup> O	KCl	Ca <sup>2</sup> O	Mg <sup>2</sup> O	Fe <sup>2</sup> O <sup>3</sup>	P <sup>2</sup> O <sup>5</sup>	SO <sup>3</sup>	SiO <sup>2</sup>	CO <sup>2</sup>	
29·02	7·13	23·76	6·70	1·63	5·47	5·04	0·98	20·27	= 100·00

**GNEISS.** A rock having the same composition as granite, but distinguished from it by possessing a partially stratified structure. In granite, the quartz, felspar, and mica, are intergrown so as to form a crystallogranular mixture; but in gneiss only the quartz and felspar are thus intergrown, whereas the mica is disposed in parallel layers, giving the rock somewhat of a slaty character. The quantitative relations of the component minerals in gneiss are as various as in granite, and the mica is often more or less replaced by hornblende or talc, less frequently by chlorite or graphite. Gneiss also contains, as accessory constituents, garnet, tourmaline, epidote, cordierite, andalusite, serpentine, cyanite, iron pyrites, magnetic pyrites, specular iron, titaniferous iron, magnetic iron ore, rutile, fluor spar; it is peculiarly rich in metalliferous veins.

For Scheerer's examination of the red and grey gneiss of the Saxon Erzgebirg, see Jahresh. d. Chem. 1861, p. 1075.

**GÖKUMITE.** See IDOCRASE.

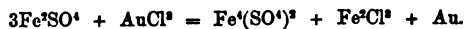
**GOLD.** Atomic weight, 196. Symbol, Au. (Gm. vi. 201.—Regnault, *Cours élémentaire de Chimie*, iii. 274.—Pelouze et Frémy, *Traité*, iii. 392.—Dana, ii. 7.—*Ure's Dictionary of Arts, Manufactures, and Mines*, ii. 381.)—Gold is widely distributed over the globe. It is almost always found native, sometimes pure, but generally more or less alloyed with silver. It occurs in the crystalline rocks, the compact metamorphic rocks, the trachytic and trap rocks, and alluvial grounds. It is sometimes found crystallised in cubes, octahedrons, and other forms belonging to the regular system, more commonly in filiform, reticulated, and arborescent shapes; also in thin laminae, often in flattened grains or scales, and in rolled masses in gravel or sand detritus. These masses, when of a certain size, are called *pepitas* or *nuggets*. In crystalline rocks, gold occurs chiefly in veins containing ores of other metals, such as iron-pyrites, copper-pyrites, galena, and sulphide of silver. In auriferous pyrites, the gold is generally present in too small a quantity to be visible when the mineral is in its natural state. Some varieties of this mineral contain not more than one five-millionth part of their weight of gold, which, nevertheless, may be profitably extracted. The greatest quantity of gold is obtained from the alluvial deposits formed by the disintegration of ancient auriferous strata. The rock deposits of California and Australia are chiefly of this kind. The sands of rivers issuing from primitive mountain chains almost always contain small quantities of gold. In Europe gold is most abundant in Hungary and Transylvania. It occurs also in the sand of the Rhine, the Reuss, and the Aar; on the southern slope of the Pennine Alps, from the Simplon and Monte Rosa to the Val d'Aosta; in Piedmont; in Spain, the mines of Asturias having been in ancient times

the principal source of the gold obtained in Europe; in many of the streams of Cornwall; near Dolgelly and other parts of North Wales; in Scotland in considerable amount near Leadhills, and in Glen Coich and other parts of Perthshire; in Ireland, in the county of Wicklow; and in Sweden, at Edelfors. In Asia valuable mines exist in the Ural mountains at Beresof, and other places on the eastern flank of the range, and in the comparatively level portions of Siberia; also in the Altai mountains, and in the Cailas mountains in Little Thibet. Gold is also found in China, Japan, Formosa, Ceylon, Java, Sumatra, Borneo, and the Philippines. In Africa there are mines at Kordofan, between Darfour and Abyssinia; also south of Sahara from Senegal to Cape Palmas; also in the interior on the Somat, a day's journey from Cassen; also along the coast opposite Madagascar, supposed to have been the Ophir of Solomon. In South America the principal gold-producing districts are in Brazil, especially near Villa Rica, and in the province of Minas Geraes; in New Granada, and in Chile. In Peru gold is found but sparingly. In Central America, gold is found in Guatemala and near Panama; in North America, in Mexico, in the Southern United States, in British Columbia along the course of the Fraser River, in Nova Scotia, and very abundantly in California, between the Sierra Nevada and the Sacramento and San Joaquin. Lastly, very large quantities of gold are found in Australia, chiefly to the westward of Bathurst, about 160 miles from Sidney, and in the Victoria colony. Gold is also found in Van Diemen's Land and New Zealand. Formerly the chief supply of gold was obtained from the mines of Brazil, Hungary, and the Ural Mountains, but California and Australia now yield by far the largest quantity. The new gold-field of British Columbia is also very productive.

The purest specimens of native gold have been obtained from Schabrowski, near Katharinenburg, in the Ural. A specimen analysed by G. Rose was found to contain 98.96 per cent. of gold. Very pure gold has also been found in Nova Scotia; a specimen from Tangier was found by Marsh (Sill. Am. J. 1861, p. 395) to contain 98.13 per cent. gold; another from Lunenburg contained 92.04 per cent., the remainder, in both cases, being silver and copper, with traces of iron. The Californian gold averages from 87.5 to 88.5 per cent., and the Australian 96 to 96.6 per cent. In some varieties of native gold, *e.g.* from Linarowski, in the Altai, the percentage of gold is as low as 60 per cent., the remainder being chiefly silver. There is also an auriferous silver found at Konigsberg, in Hungary, containing 28 per cent. gold and 62 silver.

*Extraction.*—Gold is separated from the substances with which it is mechanically associated, either by washing with water, whereby the earthy matters are carried away, while the heavy gold remains behind, or by amalgamation. The rich ores in which the native gold is apparent, and merely disseminated in a stony gangue, are directly triturated with mercury, without any preparatory treatment. The poorer ores, in which the gold seems lost amid a mass of iron, sulphide of copper, &c., are roasted before amalgamation, to lay bare the gold. The small quantity of gold which occurs, generally associated with silver, in certain lead and copper ores, is extracted by eliquation and cupellation. By these processes (see COPPER, p. 32, and SILVER) gold is obtained free from all other metals except silver; and from this it may be separated by nitric acid, which dissolves the silver, but only when it forms a large proportion of the alloy. When nitric acid does not dissolve the silver, the alloy is submitted to an operation termed *parting* or *quartation*, which consists in fusing it with four times its weight of silver, after which the whole of the silver may be dissolved out by nitric acid.

Pure gold may be obtained from any alloy containing it, by dissolving the alloy in a mixture of two measures of hydrochloric and one measure of nitric acid; separating the solution from insoluble chloride of silver by filtration; evaporating it over the water-bath till acid vapours cease to be exhaled; then dissolving the residue in water acidulated with hydrochloric acid; and adding protosulphate of iron, which completely precipitates the gold in the form of a brown or brownish-yellow powder, the protosulphate of iron being at the same time converted into sesquisulphate and sesquichloride:



The gold thus precipitated is quite destitute of metallic lustre, but acquires that character by burnishing.

From alloys of gold and silver, or of gold, silver, and copper, the gold may be separated by the action of strong sulphuric acid. The alloy, after being granulated by pouring it in the melted state into water, is heated in a platinum or cast-iron vessel with 2½ times its weight of sulphuric acid of specific gravity 1.816 (66° Baumé), the heat being continued as long as sulphurous acid is evolved. The silver and copper are thereby converted into sulphates, while the gold remains unattacked. The solution is boiled for a quarter of an hour with an additional quantity of sulphuric acid of specific gravity 1.653, or 58° Baumé (obtained by concentrating the acid mother-liquors of sulphate of copper produced in the operation), and afterwards left at rest.



The gold then settles down, and the liquid, after being diluted with water, is transferred to a leaden vessel and again boiled with sheets of copper immersed in it. The silver is then precipitated in the metallic state, while the copper is converted into sulphate, and dissolves. The gold deposited in the manner above described still retains a small quantity of silver, from which it is separated by treating it a second and a third time with strong sulphuric acid: it then retains only 0.005 of silver. This process is not applicable to alloys containing more than 20 per cent. of gold. Richer alloys must first be fused with the requisite quantity of silver. It is applicable on the large scale to the extraction of gold, chiefly from alloys which contain but a little of that metal, such as native silver and old silver coins, and, as now practised, is economically available even when the amount of gold does not exceed one part in 2000.

Some specimens of Australian gold contain 2 or 3 per cent. of tin or antimony, both. Gold thus alloyed is brittle, and not fit for rolling. The best mode of removing the tin and antimony is to oxidise them by fusing the impure gold with about 10 per cent. of oxide of copper and a small quantity of borax: a perfectly malleable gold is then obtained, containing a small percentage of copper. (Warington, Chem. Soc. Qu. J. xiii. 34.)

**Properties.**—Gold is the only metal of a yellow colour. When pure, it is more malleable than any other metal, and nearly as soft as lead. Its ductility appears to have scarcely a limit. A single grain of gold has been drawn into a wire 500 feet in length, and this metal is beaten out into leaves which have not more than 1-200,000th of an inch of thickness. The coating of gold on gilt silver wire is still thinner. Gold, when very thin, is transparent, thin gold leaf appearing green by transmitted light. The green colour passes into a ruby-red when highly attenuated gold is heated: in the red gold-glass, the gold is in the metallic state. (Faraday.)

The density of gold varies from 19.258 to 19.367, according as it has been more or less compressed. Its specific heat, referred to water as unity, is 0.324 (Regnault). Its heat-conducting power (silver = 100) is 53.2 (Wiedemann and Franz); and its electric conducting power (silver = 100) is 59.0 (Riess), 64.9 (Becquerel), 58.5 (Lenz), 55.19 at 21.8° C. (Matthiessen.)

Gold melts at 1200° C. (2192° F.) according to Pouillet; at 1380° C. (2518° F.) according to Guyton-Marveau; at 1425° C. (2596° F.) according to Daniell; it contracts considerably on becoming solid. Like most other metals, it is volatile at high temperatures. It was formerly supposed that the heat of a powerful burning-glass, or of the oxy-hydrogen blow-pipe, was required to volatilise gold, but from the experiments of Napier (Chem. Soc. Qu. J. x. 229; xi. 168) and Makins (*ibid.* xi. 97), it appears that the volatilisation takes place when alloys of gold and silver are cupelled with lead in an ordinary muffle-furnace. Deposits taken from the chimney of a small reverberatory furnace in which an alloy of silver and copper containing a very small proportion of gold had been cupelled almost daily for months together, were found to contain, on the average, about 14 per cent. of silver, and 7.1 grains of gold per mark (8 oz.) of silver.

Gold does not oxidise or tarnish in the air at common temperatures, or even when strongly ignited, but, like the other noble metals, it is dissipated and perhaps partially oxidised when a powerful charge of electricity is sent through thin leaves or wires of it (p. 396). Gold is not dissolved by nitric, hydrochloric, or sulphuric acid, or indeed by any single acid. It is acted upon by chlorine, which converts it into the trichloride, and by acid mixtures, such as nitromuriatic acid, which evolve chlorine.

**Compounds of Gold.**—Gold forms two series of compounds, viz. the *Aurous compounds*, in which it is monatomic, and the *Auric compounds*, in which it is triatomic. In its chemical relations it exhibits rather a chlorous than a basylous character, so that its oxides tend to unite with bases rather than with acids, and its chlorides and iodides readily form double salts with the chlorides and iodides of the more basylous metals.

**GOLD, ALLOYS OF.** Gold unites with nearly all metals; but its most important alloys are those which it forms with *silver* and *copper*. Gold which is used for coins, watches, articles of jewellery, &c., is always alloyed with copper, to increase its hardness, pure gold being much too soft for any of these purposes. The standard for coin in the United Kingdom is 11 gold with 1 alloy; in France and the United States of America, 9 gold to 1 alloy. For articles of jewellery gold is also frequently alloyed with silver, which gives it a lighter colour. The alloys of gold, both with silver and with copper, are more fusible than gold itself. The solder used for gold trinkets is composed of 5 parts gold and 1 part copper, or of 4 parts gold, 1 part copper, and 1 part silver.

It has already been observed (p. 925) that native gold almost always contains silver varying in proportion from 0.2 to 62 per cent. The *electrum* of the ancients is a

alloy of gold and silver, containing, according to Klaproth, 66·7 per cent. gold, or 2 gold to 1 silver.

**Amalgam of Gold.**—Gold unites readily with mercury, forming a white amalgam ; the smallest quantity of mercurial vapour coming in contact with gold is sufficient to turn it white. Mercury is capable of dissolving a large quantity of gold without losing its fluidity, but when quite saturated it acquires a waxy consistence. When the liquid amalgam is strained through chamois-leather, mercury passes through, together with a very small quantity of gold, and there remains a white amalgam, of pasty consistence, containing about 2 parts of gold to 1 part of mercury. By dissolving 1 part of gold in 1000 parts of mercury, pressing through chamois-leather, and treating the residue with dilute nitric acid at a moderate heat, a solid amalgam,  $\text{Au}^{\frac{1}{2}}\text{Hg}^{\frac{1}{2}}$ , is obtained, which crystallises in shining four-sided prisms, retains its lustre in the air, is not decomposed by boiling nitric acid, and does not melt even when heated till the mercury volatilises. (T. H. Henry, *Phil. Mag.* [4] ix. 468.)

A native amalgam of gold,  $\text{Au}^{\frac{1}{2}}\text{Hg}^{\frac{1}{2}}$ , is found in small yellowish crystals of specific gravity 15·47 in the native mercury of Mariposa in California (gold, 39·02—41·63 per cent., mercury, 60·98—58·37). An amalgam of gold and silver is found in small white soft grains accompanying platinum, at Choco, New Granada. It contains 38·39 per cent. gold, 5·00 silver, and 57·40 mercury, agreeing nearly with the formula  $(\frac{1}{2}\text{Au})^{\frac{1}{2}}\text{Hg}^{\frac{1}{2}}$ . (*Rammelsberg's Mineralchemie*, p. 10.)

**Gilding.**—The pasty amalgam of 2 parts of gold and 1 part mercury is used for gilding ornamental articles of copper and bronze. The surface of the object is first thoroughly cleaned by heating it to redness, then plunging it into dilute sulphuric acid, and sometimes for an instant also into strong nitric acid ; it is then *amalgamated* by washing it with a solution of nitrate of mercury, and afterwards pressed upon the pasty amalgam, a portion of which adheres to it. The mercury is then expelled by heat, and the gold-surface finally polished. Silver may be gilt by similar processes.

Articles of copper, chiefly copper trinkets, are also gilt by immersion in a boiling solution of chloride of gold in an alkaline carbonate, after having been cleaned by processes similar to those just described.

But the process now most generally adopted is that of *electro-gilding*, which is performed by immersing the objects to be gilt in a solution of 10 parts of cyanide of potassium and 1 part of cyanide of gold in 100 parts of distilled water, and connecting them with the negative pole of a voltaic battery, while the positive pole is connected with a bar of gold also immersed in the liquid. The solution is then decomposed by the current, the gold being deposited on the objects at the negative pole, while the gold connected with the positive pole dissolves and keeps the solution at a nearly uniform strength. (See *CYANIDES*, p. 213.) The cyanide of potassium in the solution is sometimes replaced by ferrocyanide of potassium, and the cyanide of gold by sesquioxide of gold, chloride of gold and potassium, or sulphide of gold ; but the composition above given is that which is most generally adopted. This mode of gilding may be at once applied to copper, brass, bronze, silver, or platinum. To gild iron, steel, or tin, it is necessary first to deposit a layer of copper on the surface, which is effected by immersion for a few seconds in a bath of cyanide of copper and potassium. (See *Ure's Dictionary of Arts, &c.*, art. *ELECTRO-METALLURGY*, ii. 95.)

**GOLD, BROMIDE OF,  $\text{AuBr}^3$ ,** is produced by dissolving gold in bromine-water, or in a mixture of nitric and hydrobromic acids. It greatly resembles the trichloride, crystallises with tolerable facility, and forms, with the more basic metallic bromides, a series of double salts called *bromo-aurates*, e. g. *bromo-aurate of potassium*,  $\text{KCl}.\text{AuBr}^3$ .

**GOLD, CHLORIDES OF.** The *Protochloride*, or *Aurous chloride*,  $\text{AuCl}$ , is obtained by evaporating a solution of the trichloride to dryness, heating the residue to about the melting point of tin, and constantly stirring it as long as chlorine is evolved. It is a white saline mass, having a tinge of yellow, and quite insoluble in water. In the dry state it is permanent, but in contact with water, it is resolved—gradually at ordinary temperatures, instantaneously at the boiling-heat—into metallic gold and the trichloride.

**Trichloride of Gold or Auric Chloride,  $\text{AuCl}^3$ .**—This compound is formed when gold is dissolved in nitromuriatic acid. The solution is yellow, and becomes paler with an excess of acid, but is of a deep red when neutral in composition. It is obtained in the last condition by evaporating the solution of gold, till the liquid is of a dark ruby colour, and begins to emit chlorine. It forms on cooling a dark red crystalline mass, which deliquesces quickly in air. But the only method of procuring auric chloride perfectly free from acid salt, is to decompose aurous chloride with water. An *acid chloride of gold* or *chloride of gold and hydrogen*, crystallises easily from an acid



solution, in long needles of a pale yellow colour, which are permanent in dry air, but run into a liquid in damp air. The solution of this salt (ordinary gold-solution) deposits gold on its surface, and on the side of the vessel turned to the light. The gold is also precipitated in the metallic state by phosphorus, by most metals, by ferrous salts, by arsenious and antimonious acids, and by many vegetable and animal substances, by vegetable acids, by oxalate of potassium, &c., carbonic anhydride then escaping. Sulphuric acid and sulphide of ammonium throw down black sulphide of gold, soluble in excess of the latter reagent. Ammonia and carbonate of ammonium produce a yellow precipitate of fulminating gold. Potash added in excess forms no precipitate, unless it contains organic matter, in which case a slight precipitate of aurous oxide is produced. Cyanide of potassium produces a yellow precipitate soluble in excess. Ferrocyanide of potassium colours the solution emerald-green. Stannous chloride produces a purple or brown precipitate (purple of Cassius), varying in colour according to the strength of the solutions and the proportions in which they are mixed. This reaction will indicate by a faint colouring the presence of 1 pt. of gold in 64,000 pts. of liquid. Trichloride of antimony produces a shining yellow precipitate of metallic gold. Iodide of potassium colours the liquid black, and then throws down a greenish precipitate of auric iodide. Tincture of galls throws down metallic gold.

Trichloride of gold is soluble in ether and in some essential oils. It unites with most other chlorides, forming double salts called chloro-aurates, which are almost all orange-coloured when crystallised; in efflorescing, they acquire a lemon-yellow colour, but in the anhydrous state they are of an intense red. They are obtained by evaporating the mixed solutions of the two salts.

Chloro-aurate of potassium,  $2(\text{KClAuCl}_2) \cdot 5\text{H}_2\text{O}$ , crystallises in striated prisms with right summits, or in thin hexagonal tables, which are very efflorescent; it becomes anhydrous at  $100^\circ \text{C}$ . The anhydrous salt fuses readily when heated, but loses chlorine and becomes a liquid, which is black while hot, and yellow when cold. It is then a compound of aurous chloride with chloride of potassium. Chloro-aurate of ammonium crystallises in transparent prismatic needles, which become opaque in air. Johnston found their composition to be  $\text{NH}_4\text{ClAuCl}_2 \cdot \text{H}_2\text{O}$ . Chloro-aurate of sodium crystallises in long four-sided prisms, and is permanent in air. Its composition is  $\text{NaClAuCl}_2 \cdot 2\text{H}_2\text{O}$ . Bonsdorff has prepared similar double salts with the chlorides of barium, strontium, calcium, magnesium, manganese, zinc, cadmium, cobalt, and nickel. The calcium-salt contains three, and the magnesium-salt six, atoms of water.

Trichloride of gold likewise forms crystalline double salts with the hydrochlorates of many organic bases, e. g. chloro-aurate of ethylamine,  $\text{C}_2\text{H}_5\text{N} \cdot \text{HClAuCl}_2$ ; and these gold-salts are in many instances more convenient than the corresponding platinum-salts for fixing the composition of the organic base, because they are less liable to decomposition. (Hofmann.)

#### GOLD, CYANIDES OF. (See CYANIDES, p. 212.)

**GOLD, DETECTION AND ESTIMATION OF.** 1. *Reactions.*—Gold-compounds heated on charcoal with borax or carbonate of sodium in the inner flame yield a yellow, very malleable button of metallic gold.

For the reactions of gold in solution see *Trichloride of Gold* above.

2. *Estimation and Separation.*—Gold is always estimated in the metallic state. It is generally precipitated from its solution in nitromuriatic acid by protosulphate of iron or oxalic acid. Protosulphate of iron throws down the gold in the form of a fine brown powder. If the gold-solution is quite neutral, it must be first acidulated with hydrochloric acid; otherwise the precipitated gold will be contaminated with ferric oxide formed by the action of the air on the ferrous sulphate. If the gold-solution contains much free nitric acid, there is a risk of some of the precipitated gold being redissolved by the nitromuriatic acid present. To prevent this, the excess of nitric acid must be destroyed by adding hydrochloric acid and boiling, before the iron-solution is added. Oxalic acid reduces gold slowly but completely; the gold-solution must be digested with it for 24 or 48 hours.

These methods of precipitation serve to separate gold from most other metals. In such cases, oxalic acid is mostly to be preferred as the precipitating agent, because, when the quantities of the other metals are also to be determined, the presence of a large amount of iron in solution is very inconvenient.

The separation of gold in alloys may generally be effected by dissolving out the baser metals with nitric, or sometimes with hydrochloric or sulphuric acid. When, however, the proportion of gold is considerable, it may happen that the alloy is but very slowly attacked by nitric acid, especially if the other metal be silver or lead. In such a case, it is best to treat the alloy with nitromuriatic acid, and precipitate the gold with oxalic acid. Or, again, the alloy may be fused with a known weight of lead or silver, as in the method of quartation (p. 923), and thereby rendered decomposable by nitric acid. To separate gold from tin, H. Rose (Pogg. Ann. cxii. 163) boils the finely



divided alloy with rather strong sulphuric acid mixed with hydrochloric acid; heats the liquid till the acid is partly volatilised; precipitates with water; and dissolves out the stannic oxide by means of strong hydrochloric acid, the gold then remaining.

The analysis or *assay* of an alloy of gold and copper is usually made by cupellation with lead. The weight of the button remaining on the cupel gives directly the amount of gold in the alloy after certain corrections. Alloys containing both silver and copper are cupelled with lead and a quantity of silver sufficient to bring the proportion of gold and silver in the alloy to 1 pt. gold and 3 pts. silver. The button obtained by cupellation then consists of an alloy of gold and silver, from which the silver may be dissolved out by nitric acid. (See GOLD-ASSAY, p. 932.)

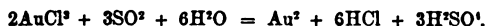
Small ornamental articles, which would be destroyed if submitted to any of the preceding processes, are approximately assayed by rubbing them on a peculiar kind of black stone, called the *touchstone*, so as to leave a streak of metal, the appearance of which may be compared with that of similar streaks produced from alloys of known composition. A further comparison is obtained by examining the appearance which the streaks present when treated with acids. This method is also sometimes used in the assaying of coins, to afford an indication of the quantity of silver required in the cupellation. The touchstone, which is a peculiar kind of bituminous quartz, was originally obtained from Lydia; but stones of similar quality are now found in Bohemia, Saxony, and Silesia.

3. *Atomic weight of gold.*—Berzelius determined the atomic weight of this metal:

1. By precipitating it from the trichloride with metallic mercury. In two experiments, 9.355 pts. gold were precipitated by 14.29 pts. mercury, and 6.557 pts. gold by 9.95 mercury. Assuming  $Hg = 100$ , and calculating from the equation  $AuCl_3 + 3Hg = 3HgCl + Au$ , the mean of these results gives for the atomic weight of gold the number 198.25.

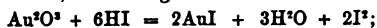
2. By the analysis of chloro-aurate of potassium,  $KClAuCl_2$  (Berz. Jahresb. xxv. 41). The salt was reduced by ignition in a stream of hydrogen; the residue of gold and chloride of potassium was weighed; the chloride of potassium then dissolved out by water; and the weight of the gold determined. Assuming the atomic weight of chloride of potassium to be 74.6, the mean of five experiments gave for gold the number 198.32.

Levol (Ann. Ch. Phys. [3] xxx. 356) determined the atomic weight of gold by dissolving a weighed quantity of the metal in nitromuriatic acid, removing the nitric acid by repeatedly boiling down the solution with hydrochloric acid, then passing sulphurous acid gas through it, and precipitating the resulting sulphuric acid with the solution of a barium-salt; 3 at. sulphate of barium thus produced correspond to 2 at. gold, thus:



From 1 gramme of gold Levol obtained 1.782  $BaSO_4$ , whence, if  $BaSO_4 = 116.48$ , the atomic weight of gold is found to be very nearly 196, which is the number now generally adopted.

**GOLD, IODIDES OF.** *Aurous Iodide*,  $AuI$ , is formed by the action of hydriodic acid on auric oxide, water being formed and two-thirds of the iodine set free:

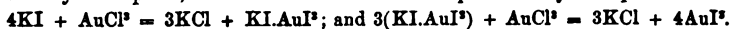


also by adding iodide of potassium in equivalent proportions, and in successive small quantities, to an aqueous solution of auric chloride:



It is a lemon-yellow crystalline powder, insoluble in cold water, and very sparingly soluble in boiling water.

*Auric Iodide*,  $AuI_3$ , is formed by gradually adding a neutral solution of auric chloride to a solution of iodide of potassium. The liquid then acquires a dark green colour, and yields a dark green precipitate of auric iodide, which redissolves on agitation; but after 1 at. of the auric chloride has been added to 4 at. iodide of potassium, a further addition of the gold-solution decolorises the liquid, and forms a permanent precipitate of auric iodide, because the iodide of gold and potassium at first produced is thereby decomposed. The successive actions are represented by the equations:



Auric iodide is a very unstable compound. When exposed to the air at ordinary temperatures, it is gradually converted into yellow aurous iodide, and afterwards into metallic gold. It combines with hydriodic acid, and with the more basic metallic iodides, forming double salts, called *iodo-aurates*:  $MI_3 \cdot AuI_3$ .

The *potassium-salt*,  $KI_3 \cdot AuI_3$ , produced by dissolving auric iodide in aqueous iodide of potassium, or by adding 1 at. auric chloride to 4 at. iodide of potassium in solution

and leaving the liquid to crystallise, forms long, slender, black, four-sided prisms, dihedral summits, and having the lateral faces striated; they have a strong lustre and are opaque even by candle-light. They give off iodine when heated, and a skeleton of gold together with iodide of potassium. In pure water they dissolve, partial decomposition; aqueous hydriodic acid and iodide of potassium dissolve perfectly.

**GOLD, MANNHEIM.** A brass containing about 4 parts copper to 1 part zinc. (See COPPER, ALLOYS OF, p. 47.)

**GOLD, MOSAIC.** An alloy of copper and zinc containing about equal parts of the two metals. (See COPPER, ALLOYS OF, p. 47; also *Ure's Dictionary of Arts*, &c. ii. 398.)

**GOLD, METALLURGY OF.** See p. 923, and for further details, *Ure's Dictionary of Arts*, &c. ii. 396.

**GOLD, OXIDES OF.** *Aurous Oxide*,  $\text{Au}^2\text{O}$ , is obtained as a green powder by decomposing auric chloride with cold potash-solution. It is partly dissolved by alkali, and soon begins to decompose, being resolved into auric oxide and metallic gold, which is deposited on the sides of the vessel as a thin film, appearing green by transmitted light, like gold-leaf.

*Auric Oxide*,  $\text{Au}^3\text{O}_3$ .—This oxide is precipitated from the solution of the chloride by alkalis; but the precipitate always retains a portion of the alkali, and is difficult to remove. A good method of preparing it is to digest magnesia or oxide of zinc in the solution of the chloride, and decompose the resulting magnesium compound with cold nitric acid (Pelletier). Frémy (*Ann. Ch. Phys.* [3], xxxi. 4) recommends the following process:—The solution of the trichloride is mixed with sufficient quantity of potash to redissolve the precipitate first produced, and boiled a quarter of an hour, whereupon the liquid, which is at first dark brown, gradually assumes a yellow tint; sulphuric acid is then added in slight excess; and the resulting precipitate is collected on a filter, and washed with water till the wash-water no longer gives a precipitate with barium-salts. The precipitate consists of auric oxide. The first addition of the potash converts the chloride of gold into an oxychloride, which then forms a soluble compound with the potash; and if the solution be treated with acid without previous boiling, a precipitate is obtained consisting of the oxychloride, which may be distinguished from the auric oxide by dissolving slowly, but completely in pure water. It is only by continued boiling that the compound of the oxychloride with potash is converted into the aurate of potassium, the conversion being attended with the change of colour above noticed. The auric oxide obtained in the manner described is not quite free from potash, even after long-continued washing. It may be purified completely by treating it with very strong nitric acid, which dissolves readily—mixing the solution with water, which immediately precipitates the auric oxide—and washing the precipitate thoroughly with pure water.

Auric oxide dried at  $100^\circ \text{C}$ . is a brown-black powder, or a brown mass having conchoidal fracture. When exposed to light, particularly to the direct rays of the sun, it is very quickly reduced. It is also decomposed by an incipient red heat. Hydrochloric acid is the only acid which dissolves and retains this oxide, and then trichloride of gold is formed. It is dissolved by concentrated nitric and sulphuric acids, but precipitated from these solutions by water. On the other hand, it possesses decided relations, its affinity for alkaline oxides being so great that, when boiled in a solution of chloride of potassium, it is dissolved, the liquid becomes alkaline, and *aurate of potassium*,  $\text{K}^2\text{O}.\text{Au}^3\text{O}_3$ , or  $\text{AuKO}^2$ , is formed. The aurates of the alkali-metals and alkaline earth-metals are nearly colourless, and are not decomposed by water.

*Aurate of ammonium. Fulminating gold.*—When a solution of gold is precipitated by a small quantity of ammonia, a powder of a deep yellow colour is obtained, which is a compound of aurate of ammonium with a portion of the trichloride of gold. This compound explodes by heat, but the detonation is not strong. But when the solution of gold is treated with an excess of ammonia, and the precipitate well washed by ebullition in a solution of ammonia, or better in water containing potash, the fulminating gold has a yellowish-brown colour with a tinge of purple, and when it explodes very easily with a loud report, accompanied by a feeble flame. It may be exploded by a heat a little above the boiling point of water, or by the blow of a hammer. Its composition has not been exactly determined, but if the ammonia is present in double the proportion that would contain the hydrogen necessary to be the oxygen of the auric oxide, which Berzelius considers probable, its constitution may be  $\text{Au}(\text{NH}^4)\text{O}^2.\text{NH}^3$  or  $\text{AuHO}^2.2\text{NH}^3$ . The affinity of auric oxide for ammonia is so great, that it takes that alkali from all acids. Thus, when auric oxide is digested in sulphate of ammonium, fulminating gold is formed, and the liquid becomes acid.

*Aurate of potassium*,  $\text{K}^2\text{O}.\text{Au}^3\text{O}_3.6\text{H}^2\text{O}$ , or  $\text{AuKO}^1.3\text{H}^2\text{O}$ , is obtained in



crystalline state by evaporating a solution of auric acid in a slight excess of pure potash, first over the open fire and afterwards in vacuo: the crystals may be freed from adhering potash by recrystallisation from water, then drained on unglazed porcelain and dried in vacuo. Aurate of potassium is very soluble in water, and forms a yellowish strongly alkaline solution, which is decomposed by nearly all organic bodies, the gold being precipitated in the metallic state: it is also decomposed by heat. With most metallic salts it forms precipitates of aurates, which are insoluble in water, but soluble in excess of the precipitant; thus, chloride of calcium forms a precipitate of aurate of calcium, soluble in excess of chloride of calcium. The solution of aurate of potassium may be used as a bath for electro-gilding.

*Aurosulphite of Potassium*,  $\text{AuKO}^2.4\text{KHSO}^2.4\text{H}^2\text{O}$ , is deposited in beautiful yellow needles when sulphite of potassium is added drop by drop to an alkaline solution of aurate of potassium. It is nearly insoluble in alkaline solutions, but dissolves with decomposition in pure water, especially if hot, giving off sulphurous anhydride and depositing metallic gold. Acids decompose it in a similar manner. After drying in vacuo, it may be preserved for two or three months, in well closed bottles, but ultimately decomposes, giving off sulphurous anhydride, and leaving metallic gold and sulphate of potassium. The same decomposition takes place more quickly when the salt is heated. (Frémy, Ann. Ch. Pharm. lvi. 315.)

A purple oxide of gold, intermediate in composition between the protoxide and trioxide, probably  $\text{AuO}$ , is produced by the action of certain reagents, *e. g.* dichloride of tin and organic substances on solutions of gold. Chloride of gold stains the skin purple, probably in consequence of the formation of this oxide.

**GOLD, OXYGEN-SALTS OF.** The oxides of gold show but little tendency to unite with oxygen-acids. The trioxide dissolves in strong nitric acid, but the solution is decomposed by evaporation or dilution. Two double hyposulphites of gold and sodium are known:

*Sodio-aurous Hyposulphite*.  $\text{Au}^2\text{S}^2\text{O}^3.3\text{Na}^2\text{S}^2\text{O}^3.4\text{H}^2\text{O}$ , or  $\left\{ \begin{smallmatrix} (\text{S}^2\text{O}^3)^2 \\ \text{Na}^2\text{Au} \end{smallmatrix} \right\} \text{O}^4.2\text{H}^2\text{O}$ .—This

salt is prepared by mixing concentrated solutions of trichloride of gold and hyposulphite of sodium, and precipitating with alcohol. When purified by repeated solution in water and precipitation by alcohol, it forms delicate, colourless needles. It has a sweetish taste, is very soluble in water, but sparingly in alcohol. It is decomposed by heat and by nitric acid, with deposition of metallic gold. Its solution gives a blackish precipitate with sulphydric acid and soluble sulphides. The presence of gold in this solution is not indicated by ferrous sulphate, stannous chloride, or oxalic acid; and, on the other hand, sulphuric acid, hydrochloric acid, and the vegetable acids, neither precipitate sulphur nor expel sulphurous acid from it. When mixed with chloride of barium, it yields a gelatinous precipitate of *baryto-aurous hypo-*

*sulphite*, containing  $\left\{ \begin{smallmatrix} (\text{S}^2\text{O}^3)^2 \\ \text{Ba}^2\text{Au} \end{smallmatrix} \right\} \text{O}^4$ . Sulphuric acid removes all the baryta from this salt, and leaves *hydrated aurous hyposulphite*, which is uncrystallisable, strongly acid, and tolerably stable at ordinary temperatures. The solution of the sodium-salt is used for fixing daguerreotype pictures. (Fordos and Gélis, Ann. Ch. Phys. [3] xiii. 394.)

A *sodio-auric hyposulphite* appears also to be formed by dropping a neutral solution of chloride of gold into aqueous hyposulphite of sodium. (Fordos and Gélis.)

**GOLD, PHOSPHIDE OF.** Gold unites readily with phosphorus by the dry way, forming a pale yellow compound more fusible than gold. Phosphuretted hydrogen passed into a solution of gold forms a precipitate of metallic gold, which then absorbs phosphuretted hydrogen, and changes to a black non-metallic mass containing phosphorus.

**GOLD, SULPHIDES OF.** *Aurous Sulphide*,  $\text{Au}^2\text{S}$ , is formed when sulphydric acid gas is passed into a boiling solution of the trichloride of gold. It is dark-brown, almost black. Aurous sulphide combines with the protosulphides of potassium and sodium, forming double salts containing 1 at. of aurous sulphide with 1 at. of the alkaline sulphide. The *sodium-salt* is obtained by fusing together 2 at. protosulphide of sodium, 1 at. gold, and 6 at. sulphur; digesting the fused mass in water; filtering the yellow solution in an atmosphere of nitrogen; and concentrating in vacuo over sulphuric acid. Yellow crystals are then obtained, having the form of oblique hexagonal prisms with trilateral or quadrilateral summits, and containing  $\text{NaAuS}.2\text{H}^2\text{O}$ . They are soluble in water and alcohol. The *potassium-salt*, which is obtained in a similar manner, forms indistinct crystals. (Col. Yorke, Chem. Soc. Qu. J. i. 236.)

*Auric Sulphide*,  $\text{Au}^3\text{S}_2$ , is formed by passing sulphydric acid gas into a cold dilute solution of gold. It is a flocculent substance of a strong yellow colour, which becomes deeper by drying; it loses its sulphur at a moderate heat.



**GOLD, TELLURIDE OF.** Precipitated on mixing a solution of auric chloride with tellurhydric acid or telluride of potassium. It likewise remains as a grey, but easily fusible mass, when auric sulphotellurite,  $\text{Au}^2\text{TeS}_3$ , is heated. (Berzelius.)

**GOLD-AMALGAM.** See page 927.

**GOLD-ASSAY.** A description of the common processes of assaying, and of furnaces and other instruments employed, will be found in *Ure's Dictionary of Arts* (article ASSAYING), in *Mitchell's Manual of Assaying*, *Phillips' Metallurgy*, and many other works. We propose here to confine ourselves to a somewhat detailed account of the gold-assay process in its highest refinements, as it is at present practised by Assayers to the Royal Mint, the Bank of England, Colonial Mints, &c., thus supply as we believe, a considerable deficiency in the publications on the subject.

We think, also, that the process here described may serve as an example to analytical chemists and experimentalists, of the degree of *method* which may be introduced when many similar operations have to be frequently performed.

The gold-assayer, receiving a great number of samples of gold alloyed with copper and silver, not differing, however, very widely in composition, is required to report the exact proportion of pure gold which each sample contains. To accomplish this the ancient processes of *cupellation* and *parting* are still, and probably ever will be, used. They are as follows:—A given weight of the alloy, say, 10,000, is weighed out, and being placed in a small porous cup or cupel heated in the muffle of the furnace, melted up with a certain quantity of lead, and with about three times as much pure silver as the alloy contains of pure gold. The new alloy of gold, silver, copper, and lead, with traces, perhaps, of other metals, being now exposed at a strong red heat to a current of air, the copper, lead, &c., are gradually oxidised, and the very fusible oxide of lead, dissolving the other oxides, carries them down into the porous substance of the cupel. There remains a button of very malleable alloy, containing three parts of silver to one part of gold, which, after being laminated, is placed in boiling nitric acid. In an action which it is difficult to explain, the silver is now almost totally dissolved away, together with any other soluble metals which may be present. The gold is left as a kind of skeleton, or spongy yet coherent mass, and may be at once solidified by drying and raising to a red heat. The result of the assay is then obtained, decimal expressed, by a simple weighing.

The result, however, may, or must, be affected by numerous errors, arising from the following chief sources:—

1. Errors of weighing.
2. Loss of gold by slight absorption in the cupel, and by volatilisation.
3. Slight solution of the gold by impurity in the acid.\*
4. Impossibility of dissolving the whole of the silver from its alloy with the gold.

Of these the first depend on the balance and weights employed, and the skill of the operator; they must for the most part be eliminated by attention to the rules given under the article BALANCE. The second and third sources of error would tend to give a result slightly below the truth; the last, and by far the most important, would cause a considerable excess in the result.

All such errors may, however, be very nearly eliminated from the results of any number of assays, on condition that the process is performed with perfect uniformity in the case of all the assays, and that the total resulting error in any one case is known; for then a correction to the amount of this error can at once be applied to every other result, and the actual truth attained. Now the process can be rendered approximately uniform by arrangements afterwards described, and the constant aggregate error is at once known if such process be performed upon any one alloy of exactly known composition. Thus, suppose 10,000 parts of each of the alloys A, B, C, to give the respective results 9207, 9416, 9077, parts of gold—but let it be known that the true result for A would have been 9200 parts—then the true results for the others would have been 9409, 9070 parts. More strictly, indeed, the corrections for B and C would have been  $-7 \times 9409 \div 9200$  and  $-7 \times 9070 \div 9200$ ; but we may neglect anything less than 1 part, and use the same corrections for all alloys which are likely to be assayed together.

It still remains to be shown how a single specimen of gold of known composition can be obtained. *Perfectly pure gold* is this required standard; for if we assay 10,000 of pure gold and obtain the result—10,007, for instance, the error of the process is obviously, at least, 7 parts. It is better, however, on the score of uniformity, to weigh out about as much pure gold as the ordinary alloys usually contain, say 9200, and adding about 800 of silver, to perform the process as usual. If we get 9207 parts of

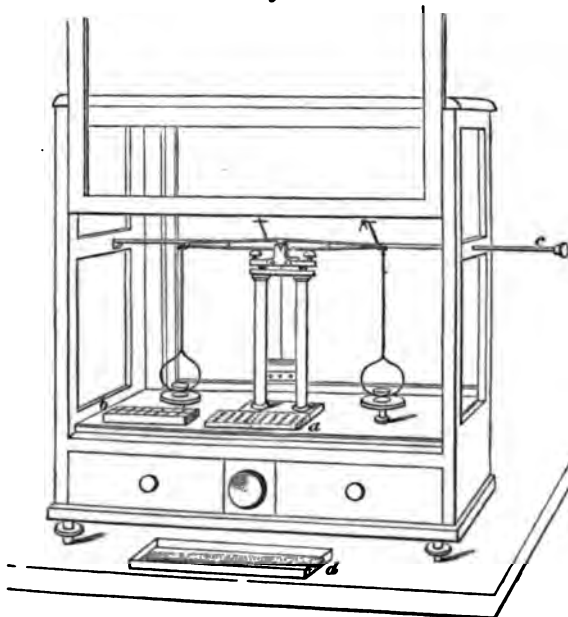
\* Nitric acid containing nitrous acid will dissolve gold (Berzelius). Now when an alloy of silver and gold is boiled in nitric acid, considerable quantities of nitrous acid are generated, and the production of this acid is still further promoted by the practice of introducing small bits of charcoal toward the end of the ebullition to prevent bumping. (Makins, Chem. Soc. Qu. J. xiii. 101.)

pure gold as the apparent result, the error of the assay is plainly seven parts. The difficulty now occurs of obtaining pure gold and proving it to be perfectly pure; but practically we attain the desired end if we assume that to be pure gold which is *the purest that can be attained by any known chemical process*. Prepare then, samples of gold of the utmost purity, and compare these against each other by numerous careful assays; assuming the purest to be absolutely pure or nearly so, the composition of each becomes known. This task too, once performed, is not again necessary so long as the specimens of pure gold last, or their standard of purity can be transmitted by sufficiently careful comparison with new samples of pure gold.

Strict uniformity of operation then, combined with the *comparison of the results* with the known purity of certain specimens of pure gold, is the mode in which alone the accuracy of large numbers of assays can be obtained. Such being the *rationale*, we now describe the practice of the process.

In the first place, the balance employed must be not only extremely sensitive and sure, but also quick, qualities which can only be combined in a very light and beautifully constructed beam. The instrument which we shall recommend is one by CErting, of Bishopsgate Street, London, with a ten-inch skeleton beam resting on an agate edge in the centre, and with very light pans suspended upon ruby points working into a small steel cross-piece (see the figure under article BALANCE). The scale-pan is loose, so that it may be taken up with the forceps and emptied of the pieces of metal it contains. It lies in a kind of stirrup formed of light elastic bands of palladium, and the weight of the whole is borne, when the balance is not in action, by an agate convex support which just touches the under surface of the stirrup. The balance, arranged exactly as in use, is shown in *fig. 518*, where at *a*, are two corner trays; *b*, a box of assay-weights; *c*, the handle of the rider movement; *d*, a file lying in a metal tray.

*Fig. 518.*

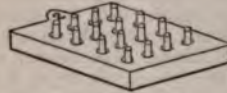


This balance when new will indicate  $\frac{1}{10,000}$  part of the assay-weight (10,000 =  $\frac{1}{2}$  grm.), and will always give  $\frac{1}{10,000}$  or 1 part correctly.

The samples of gold are received wrapped up in numbered papers, and have first to be separately flattened out with a suitable hammer and anvil to the thickness of a sixpence, each piece being carefully restored to its right paper.

Commencing with the first sample in numerical order, an assay-piece of the unit weight 10,000—the absolute weight usually adopted being  $\frac{1}{2}$  grm., or 7.717 grains—has to be weighed off each sample. The process is one entirely of trial, a small piece of alloy being cut off by a pair of hand-shears, and small pieces being repeatedly

clipped off, or added, as the beam is seen to turn one way a weight a little in excess of the 10,000 is obtained, the pan is carefully reduced by rubbing on the fine file laid i care must be taken not to file off too much, otherwise have to be made, and a repetition of the adjusting proce weighing is correct within 1 part, it may be considered allow an error of 1 or 2 parts, and to determine its amou the oscillation of the index of the balance, amounting, s either side of the zero point of the scale, and recordin number of the assay sample. This weighing process is a novice, but the practised hand may accomplish from 3 The work may be accelerated, as is often necessary, b weigh out the assay-pieces a very little above the weight of simpler construction, the chief assayer then going o the adjustment in the best balance. The small weighed order between the weighings by being placed in little gl made in the laboratory and supported in a piece of *fig. 519.*)

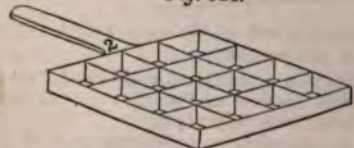
*Fig. 519.*

The assay-piece of gold thus weighed out is to be a pure lead foil  $\frac{3}{4}$ -inch square, weighing about 0.8 grm., a little metal tray with sixteen hollows, mounted on *fig. 520*). When, however, a sample of gold contains li of copper must be wrapped up in the lead-foil, namely, i other assay-pieces contain on the average.

The tray being filled with assay-packets, is carried a already containing 16 cupels arranged in square order. a piece of pure lead weighing 3.2 grms. (supposing standard gold), wrapped up in a piece of paper  $1\frac{1}{2}$ -inch s pieces of pure silver weighing in all 1.37 grm. The and the lead alloying with the silver soon forms a b oxide indeed at first appears as a solid crust, but in a and swims off the surface of the metal, which is then sa little dexterity, lead and silver may thus be placed by i sixteen cupels, beginning with the foremost on the left b them is completely melted and uncovered. The adjo explain the order of the assays both in and out of the f

1	2	3	4	13	14
5	6	7	8	9	10
9	10	11	12	5	6
13	14	15	16	1	2
Order of assays in the trays.				Order th	

When cupel (1) is ready, assay piece (1) wrapped in t tongs (the ends of which must be kept cool with water), t the bath of lead and silver, without causing any splash are similarly treated in their due order as rapidly as poss the lead-foil of each melts, and the whole of the gold i The oxidation of the lead then proceeds rapidly, and the

*Fig. 521.*

the liquid button becoming covered with an iridescent f passing off, leaves the button with a bright metallic su



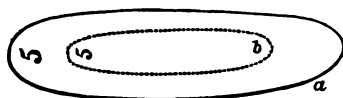
finish cupelling nearly in their numerical order, and the cupels are to be withdrawn successively from the muffle and placed in order in the sheet-iron tray (*fig. 521*).

Having become solid, each button is removed from its cupel by a pair of pliers, and any dirt remaining on its under-surface is to be removed by squeezing the button in the pliers, and brushing the bottom with a *scratch-brush* (*gratté-brosse*). Each button has now to be hammered out into the form shown in *fig. 522*, raised to a low red heat in the muffle, and then rolled out in a pair of goldsmith's rolls to the form *a* in *fig. 523*. The metallic slips have again to be annealed at a low red heat, and finally curled up into a *cornet*, as in *fig. 524*. All the sixteen assays which we suppose to be

Fig. 523.

Fig. 524.

Fig. 525.



under operation, are to be carried through these processes in company, being always kept in due order by the iron tray, except, of course, when they are in the furnace. It requires, however, some dexterity to place all the sixteen buttons or slips in the muffle in due order, and remove them again before they grow too hot and melt.

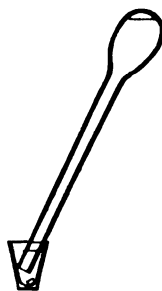
It is very necessary that the metallic slips now obtained should be smooth at the edges, and, consequently, perfectly malleable. That they are sometimes not so, may arise from the furnace being too hot or cold, the assays being too long or too short a time in it, or the quantity of lead not being correctly proportioned to the copper in the alloy.

The boiling process is now to be carried on in a row of French assay flasks, each heated by a small rose gas-burner, the fumes of the acid being carried off by an earthenware flue, or by other means. A quantity (25 grms.) of nitric acid, of the specific gravity 1.20, is to be poured into each flask from the pipette measure (*fig. 526*); one ounce measure of acid is the quantity used by many assayers. The acid is to be heated nearly to the boiling point, so that when the cornet is placed in it, violent solution of the silver at once commences. This being done, considerable heat may be applied, until in two or three minutes the whole of the orange-coloured nitrous gas is driven off. The clear acid is boiled slowly for five minutes, and then poured off into a

jug, distilled or other pure water being used to wash the adhering silver solution out of the flask. A second ounce of very pure nitric acid, of specific gravity 1.32, is now added, together with a small piece of charcoal (a calcined *pea* answers best), to prevent explosive ebullition, and the boiling of the cornet is continued as tranquilly as possible for twenty or thirty minutes. By this time the cornet will consist of a soft but coherent brownish-coloured metallic skeleton, containing the whole of the gold in the original assay piece, almost perfectly freed from silver and every other impurity. The acid is to be poured off from the *cornet*, which is done by gently inclining the flask, and the flask is filled up to the top with pure water. For this purpose it is convenient to have a small tin or copper water cistern with a stopcock, and an india-rubber tube. Each cornet must now be removed to a little crucible, which is done as in *fig. 527*, by dexterously *decanting* it—that is, inverting the flask into the crucible, allowing the cornet to fall through the water to the bottom of the crucible, and then quickly removing the flask before much water can run out. Lastly, the crucible is drained of water, and raised to a red heat in the muffle. As before, each operation is to be performed on the sixteen assays in company, before the next operation is begun, and the numerical order is always maintained mechanically.

Fig. 526.

Fig. 527.



Withdrawing the crucibles from the furnace, we find in each a small cornet of bright gold (*fig. 526*), which, if unrolled, would have the form *b* in *fig. 523*. It is then the exact counterpart of the original alloy, contracted to a much smaller size. The cornets are to be removed by a pair of weighing forceps from the crucibles, and placed in due order in the small tray (*fig. 520*). They are then to be carried back to the balance,

and successively weighed. Of course, the same pan of tin must be used as in weighing out the original assay piece of the balance. In this weighing, too, we may eliminate the error in the initial weighing (if any were observed), by adjusting the weight so that the beam shall not stand at the point of the index as it did in the prior weighing. In the ordinary series, 10,000, 5000, 2000, &c., but it is much better to use weights, as 9000, 9100, 9200, prepared by the balance expected. A rider-weight (see article BALANCE) equal in weight to the original assay piece taken, gives the result with great facility, within a few parts of the original assay piece taken.

For the purpose of correcting the results of the assays, suppose that one of the sixteen assays was what we may call a standard, performed on nearly pure gold of known standard. This gold contained 9997 pts. in 10,000 of absolutely pure gold, 9154, containing therefore very nearly 9151 pts. of pure gold assayed, giving as a result 9158. The error then of the assay is 3 pts. which amount must be subtracted from the result of each assay. This error being known or determined each day previous to the regular assays, the subtraction of the error may be done without calculation, by placing a small correction-rider on the branch of the beam, on the opposite arm to that which the rider is on, thus obtained are ready to be reported. With the same materials, this correction for *surcharge* should remain constant for months together. To ensure this constancy should be but the correctness of the results must be almost daily checked, and change in the process or materials takes place. The error is about 10 parts.

Whatever the number of assays to be done, they may be sixteen each, with proof or correction assays interspersed in the assay-book, too, may be devoted to a lot of sixteen assays, a symmetrical numerical arrangement is thus maintained, and the means; mistake or disorder is rendered nearly impossible during the process most easy and certain. Some might object to its numerical simplicity; but, in the mechanical part of the process, found comparatively awkward. In the furnacing operation, be in progress at once; but in the other parts of the process, 200 if necessary—may and ought to be performed in the furnace, hold, or gas-burners and flasks to accommodate. The apparatus and other apparatus must therefore be preserved by number, so that the last tray of any lot of assays will generally not be irregularity should be at once repeated, and, if possible, the quantities of silver and lead stated in the above table.

The quantities of silver and lead stated in the above table, English standard gold, consisting of 9167 pts. of gold and 833 of silver, varying in fineness say from 8500 to 10,000 parts, the same quantities, the variation in the resulting alloy not result materially. Each assayer must, however, estimate the quantity of silver he receives, and make the quantity of silver the weight of gold in the assay piece. The lead must be taken from the following table, to remove the largest quantity of copper in the assay piece:

Gold in 10,000 parts.	Lead, grammes.	Gold in 10,000 parts
10,000	·5	8,700
9,800	1·0	8,300
9,600	2·0	8,000
9,400	3·0	7,700
9,200	4·0	7,300
9,000	5·0	7,000

To secure uniformity, the same quantity of lead should be used in all assays, but when the gold contains much less copper than the standard, a piece of copper wire, the size of a large pin's head, must be added to the assay piece in lead-foil. This will prevent failure in the assay.

*Improved process.*—The process above described is, for the best London assayers now adopt. We have our several years a modification of the boiling process, which is more accurate, and more accurate. It is only to be recommended.

samples are pretty uniform in composition, so that proper adjustments may be made to obtain the cornets always smooth-edged and strong. In this process, each metallic slip, after lamination, is stamped with a small number at one end, as shown in *figs.* 523, 524, 525, a series of small numeral punches, from 1 to 16, being kept for this purpose. The assays from this point need no longer be kept separate. After annealing in a crucible, and coiling up as usual, each lot of sixteen is put into an English flat-bottomed assay-flask, containing say sixteen ounces of the weak acid (specific gravity 1.20), already heated over a sand-bath or gas flame. The solution and boiling proceed just as if each assay were in a separate flask. The labour of manipulation being reduced nearly to the  $\frac{1}{16}$  part, the washing with distilled water may be several times repeated, and the sixteen ounces of strong acid may be applied in two equal parts, with an intermediate washing, each portion being boiled ten minutes. Several bits of charcoal must be always in the acid to prevent bumping. The decantation is performed by filling the flask with water, closing its mouth with the thumb, inverting it into a basin full of water, and then withdrawing the thumb. The cornets fall out uninjured. By a pair of light forceps they may be safely picked out, placed in rows on a piece of tile, and annealed. The figures originally impressed on the alloy of 3 pts. of silver to 1 pt. of gold remain as legible as before, now that the 3 pts. of silver are gone; the order of the assays is thus known. Occasionally, but rarely, it may happen that a cornet is broken up, and its fragments spoil the remainder of the sixteen. Yet, having performed many thousand assays by this method, we may state that it is, on conditions already stated, not more liable to accidents than the separate method, while it is rather more speedy, effects a great and obvious saving of labour, and, by allowing perfect uniformity of action in the boiling process, admits of greater accuracy than can be otherwise attained. When the assays in the flask are less than sixteen in number, the acid used must be proportionally less; marks may easily be made on the flask with black varnish, to indicate the proper quantity of acid for each number of assays. The fumes from the flasks may easily be carried off by a  $\frac{3}{4}$  inch glass tube fitting into the mouth of the flask, and communicating with a flue. Other arrangements for supplying a good heat, as well as hot acid and hot distilled water, may easily be contrived by any person who requires to carry on the process on a large scale.

*Standard Pure Gold.*—To prepare the pure gold necessary for comparison assays, as already described, cornets or other fine gold must be dissolved in aqua-regia, and the excess of acid must be driven off as completely as possible by slow evaporation. The chloride of gold is then dissolved in a large body of pure water, say two or three gallons to each ounce of gold, and the whole left undisturbed for a week. A sediment of chloride of silver, a little insoluble subchloride of gold, and any other impurity present will then have perfectly settled down. The clear liquor is carefully drawn off by a siphon, filtered through thick paper into a perfectly clean vessel, and the precipitation of the metallic gold effected by oxalic acid, solution of protosulphate of iron, or sulphurous acid. Of these reagents we prefer the last, which is to be slowly passed through a wash-bottle and into the gold-solution, at as low a temperature as possible, and up to saturation. It is still better to precipitate the gold fractionally in three parts, of which the middle and largest part only is to be used. The soft gold powder is to be well washed, boiled in pure hydrochloric acid, again washed and dried, finally melted in a strongly heated muffle in a crucible of white French clay with a little acid sulphate of potassium and crystallised borax. Gold of at least the fineness 9997 or 9998 will generally be obtained in this way.

To perform the assays with despatch, every possible preparation must be made beforehand. The pieces of assay-lead of uniform weight may be most easily obtained by use of a bullet-mould made to cast pistol shots of the proper weight and five or six at a time.

The assay-silver must be rolled out at a flattening mill to the thickness of a fourpenny piece, and then cut up into square pieces of uniform size and of the required weight, by means of a pair of fixed shears, with an adjustable guide or gauge on the lower blade. It is necessary of course to recover the silver after its solution in the nitric acid, and use it again repeatedly. This may be done by precipitating with common salt, collecting and washing the chloride of silver, and when free from nitric acid, reducing it by pieces of zinc or iron laid in it and caused to evolve hydrogen by adding a little sulphuric acid. The metallic silver-powder which is in a little time obtained may be melted down as soon as it is cleared of the zinc or iron and the acid solution.

Much economy may be practised, if desired, in the use of the nitric acid. Thus the stronger acid (specific gravity 1.32) after being used for one assay, may be preserved, diluted with a proper quantity of distilled water, and again used as the weaker acid for another assay.

Even after being used as weak acid, the silver it contains may be precipitated by hydrochloric acid, and both the silver and nitric acid become again serviceable. The



most extreme care, however, must be taken that no nitric acid used in an assay contains the slightest trace of chlorine; otherwise gold will be dissolved and the assay entirely falsified. The presence of chlorine may of course be known by a cloudy white precipitate when silver is added to the clear liquid; but we prefer as a precaution to reverse the test, and never use any acid which does not contain a *very minute trace of silver*, and yet remain clear. If a larger quantity of silver were in the strong acid, it would, from an action not properly understood, increase the *surcharge*, or quantity of silver remaining undissolved in the cornet. By the alternate use of hydrochloric acid and silver solution, any good nitric acid may be prepared for the assay process, the chloride of silver produced, however small in quantity, being allowed entirely to subside.

The cupels used by the gold assayer should be of the finest bone-dust, made by Delenil et Fils, of Paris, who also supply, directly or through the London dealers, the best furnaces, muffles, crucibles, flasks, and other such apparatus, that is to be had. The cupels may be had ready made, or may be made in the laboratory with a proper mould. When large numbers are required, it is usual to employ a press resembling a small embossing press. Inferior English bone-earth is apt to disengage carbonic acid in the furnace, which spirits out small quantities of the melted metal and hopelessly falsifies the assay.

Of course in practice no purchase of bullion must be made on the result of a single assay, so liable as it is to accidents or mistakes; but the mean result of several assays, not differing more than ten or twenty parts among themselves, must be adopted. Thus the Bank of England carry on the whole of their enormous transactions in bullion upon triple assays of each ingot made by some scientific assayer of high standing. In every mint, two or more assayers are employed to check each other's results.

A clear idea of the accuracy of the process above described may be gained from the following table, which shows the differences of the reports of two assayers upon 1461 samples from gold ingots, each assayer making only a single assay on each.

Differ- ences.	Number of Assays differing.	Differ- ences.	Number of Assays differing.	Differ- ences.	Number of Assays differing.	Differ- ences.	Number of Assays differing.
0	123	9	28	18	1	27	1
1	257	10	29	19	1	28	2
2	240	11	28	20	2	29	2
3	205	12	15	21	4	30	1
4	156	13	11	22	2	31	2
5	117	14	8	23	2	35	1
6	79	15	7	24	0	44	1
7	65	16	8	25	6	45	1
8	52	17	1	26	2	49	1

The differences are expressed in parts of 10,000.

The mean difference of those which do not differ more than 16 parts is 3·8. Such differences arise from a want of perfect uniformity in the process. The differences beyond 16 parts obviously assume a different and unconvergent character, arising from particles of gold detached from the soft cornets; only 33 assays are thus erroneous, and these would be corrected by a repetition of the assays. Of course a difference of one part in the assay report corresponds to no more than a difference of 17. in 10,000. in the bullion transaction. The reduction of the result of an assay decimally expressed to the *trade report* in *carats, grains, and eighths*, is a simple question of arithmetic.

W. S. J.

**GOLD-BEATERS' SKIN.** The peritoneal or serous membrane separated from the intestinal tube of the ox and other animals. It is attenuated by being beaten with a hammer, and subsequently prepared so as to resist putrefaction.

**GOLD-BEATING.** See *Ure's Dictionary of Arts*, vol. ii. 398.

**GOLD-PURPLE.** *Purple or Powder of Cassius.*—When dichloride of tin is added to a dilute solution of gold, a purple-coloured powder falls, which has received these names. It is obtained of a finer tint when dichloride of tin is added to a solution of sesquichloride of iron, till the colour of the liquid takes a shade of green, and the mixture is added, drop by drop, to a solution of trichloride of gold; the liquid, in that state, is free from nitric acid, and very dilute. After 24 hours, a brown powder is deposited, which is slightly transparent, and purple-red by transmitted light, but assumes a dull blue colour when dried. Heated to redness, it loses a little water, but no oxygen, and retains its former appearance. If washed with ammonia on the filter while still moist, it is dissolved, and a purple liquid passes

through, which rivals in beauty the permanganate of potassium. From this liquid, the colouring matter separates very gradually, weeks elapsing before the upper strata of the liquid becomes colourless; but it is precipitated more rapidly when heated in a close vessel between  $140^{\circ}$  and  $180^{\circ}$  F. The powder of Cassius is insoluble in solutions of potash and soda. It may also be formed by fusing together 2 parts of gold,  $3\frac{1}{2}$  parts of tin, and 15 parts of silver, under borax, to prevent the oxidation of the tin, and treating the alloy with nitric acid to dissolve out the silver; a purple residue is left containing the tin and gold that were employed.

The powder of Cassius is certainly, after ignition, a mixture of stannic oxide and metallic gold, from which the gold can be dissolved out by nitromuriatic acid, while the stannic oxide is left; and the last mode of preparing it favours the idea that its constitution is the same before ignition; but the solubility of the unignited powder in ammonia, and the fact that mercury does not dissolve out gold from the powder when properly prepared, appear to be conclusive against that opinion. The proportions of its constituents vary so much, that there must be more than one compound; or more likely the colouring compound combines with more than one proportion of stannic oxide. Berzelius proposed the theory that the powder of Cassius may contain the purple dioxide of gold combined with sesquioxide of tin,  $\text{AuO} \cdot \text{Sn}^2\text{O}^3$ . A glance at its formula shows how readily the powder of Cassius, as thus represented, may pass into gold and stannic oxide:  $\text{AuO} \cdot \text{Sn}^2\text{O}^3 = \text{Au} + 2\text{SnO}^2$ . The existence of a purple oxide of gold,  $\text{AuO}$ , is not established; but it is probably the substance formed when a solution of gold is applied to the skin or nails, and which dyes them purple.

Pelletier gives the following method of preparing a purple of Cassius of constant composition:—20 grammes of gold are dissolved in 100 grammes of aqua-regia, containing 20 parts nitric to 80 parts of commercial hydrochloric acid; the solution is evaporated to dryness over the water-bath; the residue dissolved in water; the filtered solution diluted with 7 or 8 decilitres of water; and tin filings introduced into it: in a few minutes the liquid becomes brown and turbid, and deposits a purple precipitate, which merely requires to be washed and dried at a gentle heat. The purple thus prepared contains in 100 parts: 32.746 stannic oxide, 14.618 stannous oxide, 44.772 aurous oxide ( $\text{Au}^2\text{O}$ ) and 7.864 water. The precipitate obtained by treating trichloride of gold with pure stannous chloride is always brown. To obtain a fine purple precipitate, the chloride of gold should be treated with a mixture of stannous and stannic chlorides. The following process gives a fine purple:—*a*. A neutral solution is prepared of 1 pt. of tin in hydrochloric acid; *b*. A solution of 2 pts. of tin in cold nitromuriatic acid (1 pt. hydrochloric to 3 pts. nitric acid), the liquid being merely heated towards the end of the process that it may not contain any protoxide of tin; *c*. 7 parts of gold are dissolved in nitromuriatic acid (6 hydrochloric to 1 nitric acid), and the solution, which is nearly neutral, is diluted with 3500 parts of water. To this solution *c* the solution *b* is first added, and then the solution *a* drop by drop, till the proper colour is produced. If the quantity of *a* is too small, the precipitate is violet: if too large it is brown. It must be washed quickly, so that the liquid may not act upon it too long. (*Graham's Elements*, 2nd ed. ii. 354.)

**GOLDEN MARCASITE.** An old name of zinc. (See *Ure's Dictionary of Arts*, &c. ii. 399.)

**GOLDEN SULPHURET OF ANTIMONY.** *Sulphur Antimonii auratum.*—Pentaspilide of antimony (i. 334).

**GONG-GONG** or *Tam-tam* of the Chinese. A kind of cymbal which makes a very loud sound on being struck. It is composed of an alloy of copper and tin, containing, according to Thénard's analysis, 80 per cent. copper and 20 tin.

**GONGYLITE.** A mineral occurring in yellow or brown grains on the shore of Yli Kittajärvi, in Finland. It is indistinctly crystalline, and cleaves with moderate facility in two directions. Lustre waxy. Translucent on the edges. Streak white. Fracture conchoidal or splintery. Specific gravity = 2.7. Hardness = 4 to 5. Before the blowpipe it gives off water, and melts to a blistered glass at a stronger heat. According to Thoreld's analysis it contains:

$\text{SiO}^2$	$\text{AlO}^3$	$\text{Fe}^2\text{O}^3$	$\text{Mn}^2\text{O}$	$\text{Mg}^2\text{O}$	$\text{Ca}^2\text{O}$	$\text{K}^2\text{O}$	$\text{Na}^2\text{O}$	$\text{H}^2\text{O}$
55.22	21.80	4.80	0.32	5.00	0.77	4.46	0.45	5.77 = 98.59

which by substituting protoxides,  $\text{m}^2\text{O}$  for sesquioxides,  $\text{M}^2\text{O}^3$ , may be reduced to the general form  $(\text{M}^{\text{m}}\text{Si}^{\text{n}}\text{O}^{\text{p}})^{\text{q}}$ , which is that of a metasilicate,  $\text{R}^{\text{r}}\text{SiO}^{\text{s}}$ . (*Jahresb. d. Chem.* 1857, p. 677; *Rammelsberg's Mineralchemie*, p. 861.)

**GONIOMETER.** An instrument for measuring the angles of crystals. See *CRYSTALLOGRAPHY* (p. 169).

**GORGONIA NOBILIS.** The red coral. It consists of an interior stem, com-



posed of gelatinous matter and carbonate of calcium, with a cortex consisting of membrane with carbonate of calcium, coloured by some unknown substance. U.

**GOSHENITE.** Syn. with **BERYL**.

**GOSLARITE.** Native sulphate of zinc. (See **SULPHATES**.)

**GOSSAN.** A Cornish mining term for an oxide of iron mixed with other metals (See *Ure's Dictionary of Arts*, &c. ii. 399.)

**GOSSYPIUM.** The cotton plant. (See **COTTON**, p. 91.)

**GÖTHITE.** A variety of native ferric hydrate,  $\text{Fe}^{\text{O}^3}\cdot\text{H}^2\text{O}$  or  $\text{Fe}^{\text{O}^3}\text{HO}^2$ , crystallised in prisms belonging to the trimetric system, longitudinally striated, and often flattened parallel to the brachydiagonal. Cleavage very perfect parallel to the brachydiagonal; also fibrous, reniform, foliated, or in scales; massive. Hardness = 5 to 5.5. Specific gravity 4.0 to 4.4. Lustre imperfect adamantine. Colour yellowish, reddish, and blackish brown, often blood-red by transmitted light. Streak brownish-yellow to ochre-yellow. It is found at Eisenfeld in Nassau in foliated crystallisations of a hyacinth-red colour (*Rubinglimmer*), together with brown hæmatite. It occurs also at Clifton, near Bristol, at Lostwithiel and Botallack in Cornwall, at Lake Onega (*Onegite*) in Siberia, at Oberkirchen in the Westerwald, Zwicken in Saxony, Eisenfeld in Siegen, Przibram, &c. A capillary variety (*Sammelblende*) occurs at Przibram and elsewhere.

**GOTTHARDITE.** *Dufrenoyite*.—Native sulpharsenite of lead. It occurs crystallised in regular dodecahedrons, with truncated edges. Cleavage not distinct. Specific gravity 5.549. Lustre metallic. Colour steel-grey. Streak reddish-brown. Brittle. The mean of two analyses by Damour gave 22.39 per cent. S, 20.78 As, 55.30 Pb, 0.19 Ag, 0.26 Ca, and 0.38 Fe, agreeing nearly with the formula  $2\text{Pb}^{\text{O}^2}\cdot 8\text{As}^{\text{O}^3}\cdot \text{S}^2$ , which is analogous to that of heteromorphite, arsenic taking the place of antimony. The mineral is found in the dolomite of St. Gothard, together with realgar, orpiment, blende, and pyrites. (Dana, ii. 77.)

**GOULARD'S EXTRACT.** A saturated solution of basic acetate of lead. (See **ACETATES**, i. 16.)

**GOUTY CONCRETIONS.** Concretions of acid urate of ammonium, formerly called chalk-stones, from their resemblance to chalk. (See **URIC ACID**.)

**GRADUATED SOLUTIONS.** Solutions of acids, alkalis, &c., of known strength for volumetric analysis. (i. 255.)

**GRADUATION OF GLASS TUBES, &c.** See **ANALYSIS, VOLUMETRIC** (i. 256, 269).

**GRADUATION OF SALT WATERS.** The concentration of sea-water and the water of brine-springs previous to boiling, by causing it to fall from a trough or cistern over a wall of twigs or thorns, by which it is distributed and exposed to the air in the form of rain. (See **SODIUM, CHLORIDE OF**.)

**GRAINER.** The lixivium obtained by infusing pigeon's dung in water is used for giving flexibility to skins in the process of tanning, and is called the grainer. U.

**GRAINS OF PARADISE.** *Mallaguetta pepper*. The fruit of several zingiberaceous plants, used to give a factitious strength to beer and cordials.

**GRAIN-TIN.** See **TIN**.

**GRAMMATITE.** Syn. with **TREMOLITE**.

**GRAMMITE.** Syn. with **WOLLASTONITE**.

**GRANATIN.** *Granadin. Grenadin*.—A bitter crystalline substance, obtained by Landerer from the husks of unripe pomegranates. It crystallises in stellate groups of needles, and when heated emits the odour of burnt bread. To prepare it, the aqueous decoction of the alcoholic extract of the husks is boiled with white of egg to precipitate tannin, then evaporated; the residue is exhausted with dilute sulphuric acid, and the granatin, precipitated from the acid liquid by potash, is purified by recrystallisation.

The name granatin was also applied by Latour de Tria to a sweet substance which he obtained from the root-bark of the pomegranate tree; but this was shown by Boutron-Charlard, and Guillemette to be identical with mannite. (*Handw. d. Chem.* iii. 685.)

**GRANITE.** A crystalline rock composed of quartz, felspar, and mica, crystallised promiscuously together. The felspar constitutes ordinarily about 40 per cent., but varies very widely, while the quartz usually amounts to 30–40 per cent. Ordinary granite contains about 72.3 per cent. silica, 15.3 alumina, 7.4 alkalis, 5.0 lime, magnesia and oxide of iron. *Pegmatite* is graphic granite. [Respecting the supposed formation of granite, see **GEOLOGY, CHEMISTRY OF**, p. 832. Localities and uses of the various kinds of granite found in the United Kingdom; *Ure's Dictionary of Arts*, &c. ii. 400. On the composition of the granites of the south-west of Ireland, see a paper by the Rev. S. Haughton, *Phil. Mag.* [4] x. 23.]



**GRANULATION.** The method of dividing metallic substances into grains or small particles, in order to facilitate their combination with other substances, and sometimes for the purpose of readily subdividing them by weight.

This is done either by pouring the melted metal into water, or by agitating it in a box until the moment of congelation, at which instant it becomes converted into a powder.

Various contrivances are used to prevent danger and ensure success in the several manufactures that require granulation. Copper is granulated for making brass by pouring it through a perforated ladle into a covered vessel of water with a movable false bottom. For making small shot, a compound metal, consisting chiefly of lead, is poured into water through a perforated vessel of another kind, in which the height above the surface of the fluid requires particular adjustment. In some manufactories of this kind, the height is upward of 100 feet. U.

**GRANULITE.** *Eurite. Leptynite.*—A rock consisting of a granular mixture of felspar and quartz, sometimes with garnet.

**GRANULOSE.** According to Nägeli (*Die Stärkemehlkörner*, 1858), starch-granules consist of two substances, which may be separated by certain solvents, especially by saliva, which dissolve out the substance that gives the blue colour with iodine (the true starch, called *granulose* by Nägeli), and leave a skeleton of cellulose. Nägeli's results have, however, been called in question by other observers. (See STARCH.)

**GRAPE.** See VINE.

**GRAPE-SUGAR.** See GLUCOSE.

**GRAPHIC GOLD.** *Graphic Ore. Graphic Tellurium. Sylvanite.*—A telluride of gold and silver found at Nagyag and Offenbanya, in Transylvania. (See SYLVANITE.)

**GRAPHITE.** A variety of native carbon occurring in opaque masses of an iron black or steel-grey colour, sometimes crystalline, sometimes amorphous. (See CARBON, i. 758.)

**GRAPHITIC ACID.**  $C^{11}H^4O^3$ , or  $Gr^4H^4O^3$ .—An acid discovered by Brodie (Ann. Ch. Pharm. cxiv. 6), and produced from graphite by the repeated action of chlorate of potassium and nitric acid. Graphite, carefully purified by boiling with acids and fusion with hydrate of potassium in a silver crucible, is intimately mixed with 3 at. chlorate of potassium; the strongest nitric acid is added in sufficient quantity to render the mixture fluid; and the whole is either exposed to sunshine or heated on the water-bath to  $60^{\circ}C$ , for three or four days. If at the end of this time, no more yellow vapours are evolved, the mixture is shaken out into a large quantity of water, the undissolved portion completely washed by decantation, dried on the water-bath, and again brought in contact with the same quantities of nitric acid and chlorate of potassium; and the same treatment is repeated four times, or as often as any further alteration of the substance appears to be produced. Graphite cannot be completely converted into graphitic acid by one warming with chlorate of potassium and nitric acid, even for a long time. Graphitic acid obtained as above contains about  $\frac{1}{3}$  per cent. ash, probably derived from the glass vessels.

Graphitic acid forms perfectly transparent, thin crystals, belonging either to the trimetric or the monoclinic system. It is somewhat soluble in pure water; insoluble in water containing acids or salts. After drying at  $100^{\circ}C$ . or in vacuo, it gives, by analysis (after deducting 1.5 per cent. ash), 61.04 per cent. carbon, and 1.85 hydrogen, agreeing with the formula above given, which requires 61.01 C, 1.85 H, and 37.04 O.

*Decompositions.*—Graphitic acid decomposes when heated, with explosion, incandescence, and evolution of gas, and leaves a black finely-divided residue. When it is suspended in Rangoon naphtha (rectified over sodium and boiling at  $270^{\circ}C$ .) and heated, a large quantity of water distils over between  $100^{\circ}$  and  $200^{\circ}$ , whilst at first a small and afterwards a larger quantity of carbonic anhydride escapes, the naphtha acquires a deep red colour, and a black residue is left having the appearance of charcoal. This residue, collected after 3 or 4 hours' heating of the graphitic acid with the naphtha to  $250^{\circ}$ , weighed 66.77 to 66.98 per cent., but still contained traces of transparent crystals; after fourteen hours' heating, it weighed 65.77 per cent., and had then the composition  $C^{22}H^2O^4$ .

When a solution of *sulphydrate of ammonium* or *sulphide of potassium* is poured upon graphitic acid, it decomposes with decrepitation, forming a graphitoid substance having the metallic lustre.

Graphitic acid is decomposed in like manner by boiling with acid solutions of *cuprous* or *stannous chloride*.

*Graphitates.*—Graphitic acid unites with *alkalis*. Shaken up with *aqueous ammonia*, it is transformed into a transparent jelly, without dissolving, and on addition

of acids, is precipitated as a jelly, like silicic acid, which, after drying in *vacuo* the same weight as the graphitic acid originally employed.

*Graphite of barium*.—Moist graphitic acid, shaken up with baryta-water, washed and dried at  $100^{\circ}\text{C}$ ., yielded a compound which contained 21.19 per cent and after being suspended in water and decomposed by a stream of carbonic acid, contained at  $100^{\circ}$ , 13.30 per cent. Ba. Hence Brodie regards the former as essentially containing  $\text{C}^{11}\text{H}^3\text{BaO}^2$  or  $\text{C}^{12}\text{H}^4\text{Ba}^2\text{O}^{10}$  (calculation 24.13 per cent. Ba), and latter as  $\text{C}^{12}\text{H}^4\text{BaO}^{10}$  (calculation 13.73 per cent. Ba), and graphitic acid probably dibasic. The barium-salts are hygroscopic, and detonate with violence when heated.

**GRAPHON.** *Symbol, Gr. Atomic weight, 33.*—A modification of carbon, proposed by Brodie to exist in graphite and graphitic acid. If the latter compound regarded as analogous to the acid,  $\text{Si}^4\text{H}^4\text{O}^3$ , which Wöhler obtained by the action of oxidising agents on graphitoid silicon, it must contain 4 atoms of carbon or graphitic formula then becoming  $\text{Gr}^4\text{H}^4\text{O}^3$ , and the graphon entering into it with the atomic weight above given ( $\text{Gr}^4 = 4 \times 33 = \text{C}^{11} = 11 \times 12$ ).

**GRASSES.** The composition of cereal grasses, and of the ash which they leave when incinerated, has already been given in the article CEREALS (i. 823). The following table (p. 943) exhibits the composition of the ash of a considerable number of meadow and pasture grasses, as determined by Messrs. Way and Ogston. (Roy. Soc. J. vol. ix. pt. i.; and vol. xii. pt. ii. pp. 516, 530, 538, 539; Jahresb. d. Chem. 1850, 1855, p. 668.)

**GRASS-OIL, EAST INDIAN.** An ethereal yellow neutral oil, having a sharp agreeable taste, and an odour like that of rose-oil; it is said to be obtained from *Andropogon Iwarancusa*. By rectifying it with water, Stenhouse obtained a resinous residue, and a colourless distillate having a less agreeable odour. This distillate, after being dehydrated by chloride of calcium, began to boil at  $147^{\circ}\text{C}$ ., after which the boiling point rose to  $160^{\circ}$ , where it remained stationary for a while, and then rose higher. Analysis gave 83.76 per cent. C, 11.47 H, and 4.77 O. By treating the distillate with sodium, a brown resin was separated; and the oil decanted therefrom and again rectified, gave 88.57 per cent. C and 11.5 H, =  $\text{C}^8\text{H}^8$ .

**GRATIOLA OFFICINALIS.** According to Walz (Jahresb. pr. Pharm. xx. N. Jahresb. Pharm. x. 65), this plant contains gratioline (discovered by Marchand [J. Chim. méd. 1845, p. 357]), gratiosolin, gratiolin, several resins, tannic acid, antirrhinic acid.

*Gratioline* is a very brittle substance, insoluble in ether, slightly soluble in water, easily in alcohol, from which it separates in warty masses. It melts in boiling water. It dissolves in hydrochloric and in nitric acid, and with purple colour in sulphuric acid, the colour being destroyed by water. Potash and ammonia colour it green without dissolving it, but the colour is not permanent. The aqueous solution of gratioline is precipitated by tannic acid. (Marchand.)

According to Walz, gratioline is a glucoside, having the composition  $\text{C}^{28}\text{H}^{40}\text{O}^{17}$ , being resolved by boiling with dilute sulphuric acid into gratioletin,  $\text{C}^{11}\text{H}^{12}\text{O}^6$ , a crystallisable substance, insoluble in water and in ether, gratioleretin,  $\text{C}^{11}\text{H}^{12}\text{O}^6$ , a resinous substance, insoluble in water, but soluble in ether, and glucose (p. 869).

*Gratiosolin*,  $\text{C}^{16}\text{H}^{24}\text{O}^{13}$ , is another glucoside contained in the same plant, and easily resolved by acids, alkalis (and even oxide of lead), into glucose and gratioletin,  $\text{C}^{16}\text{H}^{24}\text{O}^{13}$ , a substance soluble in water, and precipitated by tannic acid; gratioletin is further resolved by boiling with dilute acids into glucose, and a resinous mixture of gratiosoleretin,  $\text{C}^{16}\text{H}^{24}\text{O}^{13}$ , soluble in ether, and hydro-gratioletin,  $\text{C}^{16}\text{H}^{24}\text{O}^{11}$ , insoluble in ether (p. 869). (Walz.)

**GRAULITE.** See TECTITE.

**GRAUWACKE** or *Greywacke*, is a rock composed of pieces of quartz, feldspar, slate, felspar, and clay-slate, cemented by a clay-slate basis. These pieces vary in size from a hen's egg to little grains. When the texture becomes exceedingly fine-grained the rock constitutes greywacke-slate. Its colour is usually ash or smoke-grey, with the yellowish-grey or greenish tinge frequent in primitive slate. It has not the tinuous lustre of primitive slate, but glimmers from interspersed scales of mica. It contains quartz veins, but no beds of quartz. Petrifications are found in it.

The term grauwacke formation is applied to a group of rocks between carboniferous strata and the primitive rocks, the true grauwacke being only an individual member of this group.

**GRAVITY, SPECIFIC.** See SPECIFIC GRAVITY.

**GREEK FIRE.** An inflammable compound, supposed by some to have been composed of asphaltum with nitre and sulphur, by others to have had nearly the same composition as gunpowder.

Composition per cent. of the Ash of Grasses.

Name of Grass.	Potash.	Soda.	Lime.	Magnesia.	Ferric oxide.	Sulphuric anhydride.	Silica.	Carbonic anhydride.	Phosphoric anhydride.	Chloride of Potassium.	Chloride of Sodium.	Total.	Ash in 100 pts. of fresh substance.	Ash in 100 pts. of dry substance.	Sulphur in 100 pts. of dry substance.
<b>In flower.</b>															
( <i>Anthoxanthum odoratum</i> . . . . .)	32.03		9.21	2.53	1.18	3.39	28.36	1.26	10.09	7.03	4.90	99.98	1.24	6.32	1.83
<i>Alopecurus pratensis</i> . . . . .	37.03		3.90	1.28	0.47	2.16	38.75	0.66	6.25	9.60		99.99	1.56	7.81	3.21
<i>Avena pubescens</i> . . . . .	31.21		4.72	3.17	0.72	3.37	36.28		10.82	4.05	5.66	100.00	2.01	5.22	
<i>Avena flavescens</i> . . . . .	36.06	0.73	7.98	3.07	2.40	4.00	35.20		9.31		1.25	100.00	2.54	6.18	
<i>Bromus erectus</i> . . . . .	20.33		10.38	4.99	0.26	5.46	38.48	0.55	7.53	10.63	1.38	99.99	2.11	5.21	3.45
<i>Bromus mollis</i> . . . . .	30.09	0.33	6.84	2.60	0.28	4.91	33.34	9.07	9.62		3.11	99.99	1.36	6.82	
<i>Cynosurus cristatus</i> . . . . .	24.99		10.16	2.43	0.18	3.20	40.11		7.24	11.60		99.91	2.38	6.36	
<i>Dactylis glomerata</i> . . . . .	29.52		5.82	2.22	0.59	3.62	26.65	2.09	8.60	17.86	3.09	99.96	1.59	5.31	2.37
<i>Dactylis glomerata</i> (with ripe seeds) . . . . .	33.06		8.14	3.47	0.23	3.96	32.18	2.88	6.41	4.87	4.76	99.96	2.61	5.51	2.48
<i>Festuca duruscula</i> . . . . .	31.84		10.31	2.83	0.78	3.45	28.53	1.38	12.07	8.17	0.62	99.98	1.66	5.42	
<i>Holcus lanatus</i> . . . . .	34.83		8.31	3.41	0.31	4.41	28.31	1.82	8.02	3.91	6.66	99.99	1.93	6.37	2.78
<i>Lolium perenne</i> . . . . .	24.67		9.64	2.85	0.21	5.20	27.13	0.49	8.73	13.80	7.25	99.97	2.15	7.54	3.07
<i>Annual Rye-grass</i> . . . . .	28.99	0.87	6.82	2.59	0.28	3.45	41.79		10.07		5.11	99.97	1.99	6.45	1.65
<i>Poa annua</i> . . . . .	41.86		11.69	2.44	1.57	10.18	16.03	3.29	9.11	0.47	3.35	99.99	0.59	5.83	2.18
<i>Poa pratensis</i> . . . . .	31.17		5.63	2.71	0.28	4.26	32.93	0.40	10.02	11.25	1.31	99.96	1.65	5.94	1.55
<i>Poa trivialis</i> . . . . .	29.40		8.80	3.22	0.29	4.47	37.50	0.29	9.13	6.90		100.00	2.20	8.33	
<i>Phleum pratense</i> . . . . .	24.25		14.94	5.30	0.27	4.86	31.09	4.02	11.29	0.70	3.24	99.96	2.26	5.29	
<i>Hordeum pratense</i> . . . . .	20.26	3.40	5.04	2.42	0.66	4.29	56.23		6.04		1.66	100.00	2.54	6.18	
<i>Italian Rye-grass</i> . . . . .	12.45	3.98	9.95	2.23	0.78	2.82	59.18		6.34		2.27	100.00	6.16	6.97	
<i>Do. standing in seed</i> . . . . .	10.77	0.13	12.29	2.64	0.30	1.31	60.62		6.32		5.58	99.96	5.66	6.40	
<i>Do. seeds</i> . . . . .	9.51	0.06	9.98	5.26	2.36	2.31	50.55	0.44	17.89		1.62	99.98	6.10	6.91	3.06
<b>Grass from irrigated meadow-land:</b>															
First crop . . . . .	50.00	0.09	9.50	2.47	1.31	3.55	9.24	11.62	9.31		2.91	100.00	1.28	10.37	1.97
Second crop . . . . .	22.13		9.13	2.49	0.11	4.23	34.11	1.15	5.56	17.40	3.14	99.96	2.24	8.82	3.02
Meadow hay . . . . .	3.79		12.89	3.42	0.15	0.65	63.08	0.16	4.37	6.05	5.40	99.96	6.64	7.73	1.02



**GREEN-EARTH or SELADONITE.** An altered form of augite. Celadine green, or green of various shades. Massive and in globular and amygdaloidal-shaped pieces, sometimes hollow. Dull. Fracture earthy. Opaque. Feebly glistening in the streak. Soft and sectile. Rather greasy. Adheres slightly to the tongue. Specific gravity = 2.6. Before the blow-pipe it is converted into a bluish vesicular slag.

	a.	b.	c.	d.	e.	f.
Silica . . .	52.04	60.09	51.25	53	45.87	39.48
Alumina . . .	4.93	5.28	7.25	..	11.18	10.31
Ferric oxide . . .	..	..	..	28	..	8.94
Ferrous oxide . . .	25.54	15.72	20.72	..	24.63	15.66
Magnesia . . .	4.26	4.95	6.16	2	0.28	1.70
Lime . . .	1.38	0.09	..	..	1.50	15.24 CaCO <sub>3</sub>
Soda . . .	..	2.51	1.92	..	..	..
Potash . . .	6.03	5.04	6.21	10	6.72	8.67
Water . . .	5.19	4.44	6.49	6	9.82	..
	99.37	98.12	100.00	99	100.00	100.00

Green-earth appears to have been produced from augite by the action of alkaline carbonates in solution, the change consisting in the removal of lime and magnesia and the substitution of alkalis in their place. It consists chiefly of ferrous silicate, will be seen from the preceding analyses: *a, b*, from Iceland (Waltershausen); *c*, from Mount Baldo (Delesse); *d*, from the neighbourhood of Verona (Jameson); *e, f*, from Fassa in the Tyrol. (Rammelsberg.)

It is a frequent mineral in the amygdaloid of Scotland, England, Ireland, Iceland and the Faroe Islands. It occurs also in Saxony, the Tyrol, Hungary, and near Verona. (Dana, ii. 165; Bischof's *Chemical Geology*, ii. 130, 328.)

**GREEN IRON ORE.** Native ferric phosphate. (See Iron.)

**GREEN LEAD ORE.** Arsenio-phosphate of lead with chloride of lead. (See LEAD.)

**GREEN PIGMENTS.** *Bremen green* is either a basic carbonate of copper obtained by precipitating sulphate of copper with a mixture of carbonate of soda and caustic soda or potash, or a hydrated oxide prepared by precipitating with caustic alkali alone.—*Brunswick green* is an oxychloride of copper, prepared by exposing copper foil to the air, moistening it repeatedly with hydrochloric acid or sal-ammoniac, and exhausting the product with water (i. 70).—*Chrome green* is either anhydrous chromic oxide, or a mixture of chrome-yellow with Prussian-blue (i. 934, 948).—*Cobalt green* or *Rinnmann's green*, is a mixture, or perhaps a compound, of the oxides of zinc and cobalt (i. 1057).—*Crystallised green* is neutral acetate of copper (i. 14).—*Emerald green* or *Vert pannelier* is a hydrated chromic oxide (i. 950).—*English-green* (*Vert anglais*) is a mixture of arsenite of copper with various white substances, such as sulphate of barium or calcium.—*Iris green*, a colour formerly used in miniature painting, was prepared by macerating in cold solution of alum or gum-water the satin epidermis of the petals of the iris, filtering the liquid through a fine calico, and leaving it to evaporate on plates in a shady place.—*Mineral green*. This term is now generally applied to Scheele's green, but it originally denoted a mixture of 2 pts. Scheele's green with 6 pts. white lead, 2 pts. black oxide of copper, 3 pts. malachite, and  $\frac{1}{2}$  p. acetate of lead. This mixture has an apple-green colour, with bluish reflex.—*Milori green* (*Vert en grains*) is a very fine green pigment, containing chromic acid, sulphuric acid, cyanogen, potassium, iron, and lead. Its preparation is kept secret, but it may be imitated by mixing the solutions of ferrocyanide of potassium, protosulphate of iron, acetate of lead, and bichromate of potash. A precipitate is thus obtained of a very fine green colour, but not so durable as that prepared by the inventor's process.—*Sap green* (*Vert de vessie, vert végétal*) is the juice of buckthorn berries combined with lime or alumina.—*Mittis, Vienna, or Kirchberger's green* is an arsenate of copper,  $2\text{Cu}^2\text{O} \cdot \text{As}^2\text{O}_5$ , prepared by precipitating sulphate of copper with arsenate of potassium.—*Mountain green* is green carbonate of copper, either native or prepared by precipitation (i. 783).—*Prussian green* is ferrocyanide of cobalt; it has a very rich green colour when recently prepared, but quickly turns red-grey on exposure to the air: hence it is but rarely used.—*Scheele's green* is arsenite of copper (i. 376).—*Schweinfurt green* is aceto-arsenite of copper (i. 15, 376).—*Veronese green* (*Vert à Paul Veronèse*). An arsenate of copper prepared in this country and in Alsace by a process which is kept secret.—*Zinc green*. This term is applied to cobalt or Rinnmann's green, and to a cyanide of zinc and iron obtained by macerating finely powdered Prussian blue in a strong solution of chloride of zinc. A fine colour is thus obtained, but, like all other colours formed from cyanides, it is not permanent. (See *Chimie des Couleurs*, par J. Lefort, Paris, 1855; also *Ure's Dictionary of Arts*, &c. i. 803, ii. 402.)

**GREEN VITRIOL.** Protosulphate of iron. (See SULPHATES.)

**GREENLANDITE.** Garnet from Greenland.

**GREENOCKITE.** Native sulphide of cadmium. (See CADMIUM.)

**GREENOVITE.** Syn. with SPHENE.

**GREENSAND.** This term is commonly applied to a series of beds lying between the chalk and the Wealden deposits, but is strictly applicable only to certain minor portions of them, marked by the presence of minute grains of green silicate of iron (the glauconite of American mineralogists). The upper portion of the series contains a calcareous sand, very rich in soluble silica, and forming an excellent agricultural soil. (See GLAUCONITE; also *Ure's Dictionary of Arts*, &c. ii. 402.)

**GREENSTONE** or *Diabase* is a rock composed of augite with labradorite and oligoclase. The term greenstone is also applied to certain varieties of trap, consisting of dark and heavy blackish-green or brownish rock composed of felspar and hornblende, usually having a crystalline structure, but sometimes compact. When albite (soda-felspar) replaces orthoclase (potash-felspar), the rock is called diorite. (Dana, ii. 162, 247.)

**GRENADIN.** Syn. with GRANATIN.

**GRENATITE.** Syn. with STAUROTIDE.

**GRENGESITE.** A silicate from Grengesberg in Dalecarlia, containing, according to Hisinger's analysis, 27.01 per cent. silica, 14.31 alumina, 2.18 manganous oxide, 25.63 ferrous oxide, 14.21 magnesia, and 12.53 water. It is allied to delessite. Colour dark-green. (Dana, ii. 296.)

**GREY ANTIMONY.** Native trisulphide of antimony (i. 329).

**GREY COPPER.** Syn. with TETRAHEDRITE.

**GREYWACKE.** Syn. with GRAUWACKE (p. 941).

**GREY DYE.** See DYEING (p. 359); also *Ure's Dictionary of Arts*, &c. (ii. 403).

**GROPPITE.** A silicate found in the limestone of Gropptorp, in Sweden. It is crystalline, with one distinct cleavage, affording a broad cleavage-surface, and two others less distinct. Hardness = 2.5. Specific gravity = 2.73. Thin splinters translucent. Colour rose-red to brownish-red. Streak paler. Fracture splintery. According to Svanberg's analysis (*Öfversigt af Kongl. Vetenskaps Akad. Förhandlingar*, iii. 14) it contains:

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sup>2+</sup> O <sub>3</sub>	CaO	Mg <sup>2+</sup> O	K <sub>2</sub> O.	Na <sub>2</sub> O	H <sub>2</sub> O
45.01	22.55	3.06	4.55	18.28	5.23	0.22	7.11

together with 0.13 of undissolved matter (total 100.13), whence Svanberg deduces the formula  $3MO.2Al^{2+}O_3.3\frac{1}{2}SiO_2 + 3HO$  or  $6M^{2+}O.4Al^{2+}O_3.9\frac{1}{2}SiO_2 + 6H^{+}O$ , which, by substituting  $al^{2+}$  for  $Al^{2+}$  may be reduced to  $2M^{2+}O.4al^{2+}O_3.3SiO_2 + 2H^{+}O$ , or (including M and al under the general symbol R), to  $R^{2+}Si^{2+}O_3 + 2H^{+}O$  or  $R^{2+}SiO_4 + \frac{1}{2}H^{+}O$ , which is the formula of an orthosilicate.

**GROROLITE.** A variety of Wad or Earthy Manganese, found at Groroi, in Mayenne; also at Viedessos and Cautern, in France. (See MANGANESE.)

**GROSSULAR** or *Grossulara*.—A variety of lime-garnet. (See GARNET, p. 772.)

**GRÜNAUTE** or *Nickel-bismuth glance*.—Native sulphide of nickel and bismuth, found at Grünau, near Sayn Altenkirchen, with quartz and copper pyrites.

**GRÜNERITE.** A nearly pure iron augite,  $Fe^{2+}SiO_3$ . A specimen from Collobrières, analysed by Grüner (*Compt. rend.* xxiv. 794), yielded 43.9 SiO<sub>2</sub>, 52.2 Fe<sub>2</sub>O<sub>3</sub>, 1.1 Mg<sub>2</sub>O, 0.5 Ca<sub>2</sub>O, and 1.9 Al<sub>2</sub>O<sub>3</sub> = 99.6.

**GUACIN.** A bitter substance extracted from Guaco, the leaves and stems of the *Mikania Guaco*, a plant nearly allied to the genus *Eupatorium*, growing in Mexico and South America, whence it has been imported into Europe and used as a remedy against cholera. Guacin is obtained, according to Pettenkofer, by exhausting guaco with alcohol, decolorising with animal charcoal, distilling off the alcohol, dissolving the residue in ether, and leaving the solution to evaporate. It then remains as a light brown resinous mass, perfectly soluble in alcohol, partially in water, having a very bitter taste and emetic action, and emitting an intoxicating odour when triturated with sulphuric acid. (*Handw. d. Chem.* iii. 714.)

**GUAIAIC.** See GUAIAICUM.

**GUAIAICENE.** C<sub>10</sub>H<sub>16</sub>O. *Gaiacene*. *Guajol*.—The light oil obtained in the dry distillation of guaiac resin. It is colourless, and has an agreeable odour, like that of bitter almonds. Specific gravity 0.874. Boiling point 118° C. Vapour-density 2.92. When exposed to the air it oxidises, and is converted into beautiful crystalline laminae (Deville, *Compt. rend.* xvii. 1143; xix. 134). It is not altered by caustic potash solution, or by an alcoholic solution of sesquichloride of iron (if it contains guaiacol,



the iron-solution colours it green). It is insoluble in ammonia, and does not combine with the acid sulphites of alkali-metals. It is oxidised by chromic and by nitric acid, acetic acid being produced in the former case, and oxalic acid in the latter. According to its composition, guaiacene might be regarded as the aldehyde of angelic acid ( $C^8H^8O^2$ ), but it is not converted into that acid by fusion with hydrate of potash (Gilm, Ann. Ch. Pharm. cvi. 379.)

**GUAIAICIC ACID.** See GUAIARETIC ACID.

**GUAIACOL.** *Hydride of Guaiacyl. Guaiacylous acid. Pyroguaiacic acid.* (Gm. xii. 350.—Gerh. iii. 780.—Hlasiwetz, Ann. Ch. Pharm. cvi. 361.)—Produced together with guaiacene and pyroguaiacin, by the dry distillation of guaiacum. When the crude oil obtained by this distillation is washed with water and rectified over a moderate heat, guaiacene passes over first, and afterwards, when the heat is increased, the guaiacol distils. It may be purified by repeated rectification, or, according to Völckel, by dissolving it in potash, boiling it with water as long as any light oil passes over, then mixing it with a quantity of sulphuric acid not quite sufficient to combine with the whole of the potash, redissolving the separated oil in potash, boiling the solution in a retort, till the milky oil which passes over becomes perfectly clear or colourless, addition of a small quantity of potash, again separating the oil by sulphuric acid, and drying it in *vacuo* over sulphuric acid.

Guaiacol is a colourless oil, having a specific gravity of 1.119 at 22° C. (Sobrero, 1.125 at 16° (Völckel)). It has a peculiar faint odour, somewhat like that of creosote, and a pungent peppery taste like cloves. It boils at 210° C. (Sobrero), at 212° C. (Völckel). It does not redden litmus. It burns with a white smoky flame. It is an acid, even when very dilute, attacks it violently at ordinary temperatures, forming oxalic acid and a brown resin. With chlorine and bromine it forms crystallisable substitution-products. It does not yield an acid when treated with oxide of silver, dissolving in that respect from the homologous compound furfural (p. 750), which yields pyromucic acid when thus treated. (Schwanert, Ann. Ch. Pharm. cxvi. 257.)

Guaiacol is soluble in alcohol, and sparingly soluble in water. The alcoholic solution reduces the salts of gold and silver to the metallic state, and ferric and cupric salts to ferrous and cuprous salts.

Guaiacol dissolves in potash, and combines also with other bases, forming crystallisable salts, which turn black when exposed to air and moisture. It does not decompose carbonates.

Respecting the composition of guaiacol various statements have been given. According to Völckel's analyses, it contains 68.9 per cent. carbon, 6.4 hydrogen, 24.7 oxygen; according to Sobrero, 68.7 per cent. C, 6.8 H, and 25.4 O, while Völckel deduces the formula  $C^{15}H^{10}O^4$ , and Sobrero,  $C^{15}H^{10}O^4$ . Pelletier and Dumas assign to it the more probable formula,  $C^8H^8O^2$ , or  $C^4H^4O^1$  (calculation, 67.74 per cent. C, 6.45 H, and 25.81 O), which likewise agrees nearly with the vapour-density determined by these chemists (exp. 4.49; calc. for 2 volumes, 4.30).

According to Hlasiwetz, guaiacol, obtained as above, is not a definite compound, but a mixture in variable proportions of the two homologous compounds,  $C^8H^8O^2$  and  $C^{15}H^{10}O^4$ . By agitating the purified oil with strong ammonia, or passing ammonia gas into it, pressing the resulting crystalline mass, dissolving it in warm ether, and filtering the solution in an air-tight vessel with strong alcoholic potash, Hlasiwetz obtains a white crystalline mass, consisting essentially of  $C^8H^8KO^2$ , or  $C^4H^4KO^1$ , according to the quantity of potash used. The latter salt was likewise obtained by repeatedly agitating the oil with moderately strong aqueous ammonia, washing the oil with water, separating from the watery liquid, repeatedly rectifying it, dissolving it in an equal volume of ether, and treating the solution with a slight excess of very strong alcoholic potash. On decomposing the resulting potassium-salt with oxalic or dilute sulphuric acid, a colourless oil was obtained, having an agreeable odour, and varying in boiling point from 203° to 230° C. The portion which distilled between 205° to 210° had a specific gravity = 1.117 at 13°, and exhibited nearly the composition  $C^8H^8O^2$ ; between 216° and 218°, a distillate was obtained of specific gravity 1.116 and composition  $C^{15}H^{10}O^4$ ; and between 219° and 220°, a distillate of specific gravity 1.089 and composition  $C^8H^8O^2$ .

From 205° to 210°.			From 216° to 218°.			From 219° to 220°.		
	Calc.	Exp.		Calc.	Exp.		Calc.	Exp.
C	67.74	67.95	C	68.70	68.61	C	69.56	69.56
H	6.45	6.93	H	6.87	6.93	H	7.24	7.24
O	25.81	25.12	O	24.43	24.46	O	23.20	23.20
	100.00	100.00		100.00	100.00		100.00	100.00

The formula  $C^{15}H^{10}O^4$  is exactly intermediate between the other two ( $C^8H^8O^2$  and  $C^{15}H^{10}O^4$ ). The proportions in which these two compounds (which are homologous)



with furfural,  $C^3H^4O^2$ ) are present varies with the nature of the resin from which the guaiacol is obtained. The compound  $C^3H^{10}O^2$  is likewise contained in wood-tar creosote.

**GUAIACONIC ACID.**  $C^9H^{12}O^3$ .—This acid, according to Hadelich (J. pr. Chem. cxxxvii. 321), constitutes 70·35 per cent. of guaiac resin, and remains in the mother-liquor obtained in the preparation of guaiaretic acid (p. 948). To separate it, the mother-liquor is evaporated to dryness, the residue treated with boiling alcohol, the alcoholic solution evaporated, and the remaining brittle mass treated with ether (in which it is only partly soluble). The ethereal solution when evaporated yields guaiaconic acid, as an uncrystallisable mass, melting at  $100^\circ C$ , insoluble in water, possessing lævo-rotatory power, precipitable from its alcoholic solution by barium- and lead-salts. The lead-precipitate contains  $C^{10}H^{10}Pb^2O^3$ . There is also another lead-salt containing a larger proportion of lead.

Guaiaconic acid is instantly turned blue by oxidising agents. (Hadelich.)

**GUAIACUM.** *Guaiac. Guajaharz. Resina guajaci nativa.* (Handw. d. Chem. iii. 718.—Gerh. iii. 778.—Hlasiwetz, Ann. Ch. Pharm. cvi. 361; cxii. 182.)—A resinous substance obtained from the *Guajacum officinale*, a tree growing in Jamaica, St. Domingo, and others of the West Indian Islands. It exudes spontaneously or from incisions made in the stem (*Guaiacum in granis*), and is likewise obtained by melting it out from the more resinous parts of the tree (*Gu. in massis*); the latter is impure, containing chips of wood and bark.

Guaiacum has a yellowish or reddish brown colour, and is transparent in small lumps, but is generally covered with a greenish-grey powder, which renders it opaque. It is hard and brittle, with a vitreous fracture; specific gravity = 1·205 to 1·226. Its powder is white, but soon turns green when exposed to the air. Its taste is faint at first, but soon becomes acrid and produces a burning sensation in the throat. It has scarcely any odour when cold, but when heated gives off a peculiar aromatic odour, something like that of gum benzoin; it melts easily, and at a higher temperature gives off a vapour which strongly irritates the lungs.

Alcohol dissolves about  $\frac{1}{10}$  of the resin of guaiacum, and the solution is precipitated by water. Ether and oil of turpentine likewise dissolve it, but leave a more considerable residue. In pure water it is nearly insoluble; but when its alcoholic solution is poured into a considerable quantity of cold water, the resin separates in white flakes, leaving a colourless liquid which possesses in a high degree the aromatic odour of the resin. It is immediately coloured deep yellow by a few drops of ammonia, and is again rendered colourless by acids.

Guaiacum dissolves in potash and in strong sulphuric acid. The latter solution has a splendid red colour, and yields a violet precipitate with water; alcohol first colours the liquid violet-blue, and in larger quantity imparts to it a dirty bluish-green tint (Schiff, Ann. Ch. Pharm. exi. 372). According to Kossmann (J. Pharm. [3] xxxviii. 81; Rép. Chim. pure, 1863, p. 391), it is resolved by sulphuric acid into sugar and a resinous body called *guaiaretin*.

Guaiacum is distinguished by the facility with which it oxidises and the changes of colour thereby produced. Both the powder and the alcoholic solution turn green when exposed to the air, the change taking place most quickly, according to Wollaston, under the influence of the violet rays of the spectrum, whereas the red rays restore the yellow colour. Nitrous acid colours guaiacum blue, and this reaction may be used to detect the presence of a small quantity of nitric acid in sulphuric acid. If the concentrated acid to be tested be heated in a test-tube with a small quantity of iron filings, and the vapour passed into tincture of guaiacum, a blue colour will be produced if nitric acid is present, but if the sulphuric acid is pure, no change of colour will take place (Schiff). Guaiacum is coloured green by *fuming nitric acid*, and on adding to the liquid a moderate quantity of water, a green precipitate is formed, while the liquid becomes colourless; a larger quantity of water colours the precipitate blue and the solution brown.

The alcoholic solution of guaiacum is precipitated green by *sulphuric acid* and blue by *chlorine*. Iodine added to the alcoholic tincture of guaiacum produces either a dirty greenish colour or none at all; but the liquid turns blue on addition of water. The production of this blue colour is prevented if an acid be previously added; but neutral salts do not prevent it. Tincture of guaiacum is coloured blue by *sesquichloride of iron*, and on adding to the liquid a solution of *hyposulphite of sodium*, a very fine violet colour is at first produced, but this soon disappears and leaves a colourless liquid. A solution of *sulphurous acid* which has been digested with zinc, immediately decolorises tincture of guaiacum turned blue by ferric chloride, without at first producing the violet colour. Unaltered sulphurous acid also decolorises the liquid, but much more slowly. (Schiff.)

According to Ure's analysis, guaiacum contains 67·9 per cent. carbon, 7·05 hydrogen, and 25·1 oxygen. Pelletier found, in a very pure specimen, 71·0 per cent. C, 7·03

H, and 23.97 O; Johnston, who analysed the p obtained 70.35 to 70.56 per cent. C, 6.80 to 6.87 deduced the formula  $C^{20}H^{22}O^2$ .

Guaiacum is not, however, a definite compo (Ann. Ch. Pharm. xvi. 369), it is separated by s one of which is very soluble in aqueous ammon alkali a tarry compound, which requires 6,000 pa to Pelletier, ammonia dissolves  $\frac{2}{10}$  of guaiac re a colourless crystalline resin, guaiaretic acid proportion of the whole, may be obtained by decomposing the resulting salt with hydrochloric

According to Hadelich (J. pr. Chem. lxxxvii about  $\frac{1}{10}$  of guaiac resin, and the mother-liquor about 70 per cent. of an uncrystallisable acid (gua and a resin distinguished as  $\beta$ -resin, insoluble precipitated by acids. The composition of guaiac is as follows:

Guaiaretic acid (crystallisable) . . .	.
Guaiaconic acid (uncrystallisable) . . .	.
$\beta$ -resin, $C^{14}H^{14}O^2$ or $C^{20}H^{22}O^4$ . . .	.
Gum . . . . .	.
Woody matter . . . . .	.
Fixed constituents insoluble in water,	
Guaiacic acid, colouring matter, and loss	

The colouring matter, which contains nitrogen, drons on saturating with acetic acid the liquor milk of lime. It is a weak acid, soluble in alkali lead; soluble also in alcohol and ether, very s colour is deepened by alkalis. The colouring m sulphuric acid dissolves it with deep blue col (Hadelich.)

Guaiacum subjected to dry distillation yields . On rectifying the crude distillate, the guaiacene j at higher temperatures, and the pyroguaiacin is distillate.

Guaiaretic acid subjected to dry distillation y guaiacol.

**Pyroguaiacin** is a crystalline substance, alcohol. From the latter solution, it separates i a reddish colour. It melts at  $183^\circ$  C., and soli strongly heated, it volatilises and forms a cry With *nitric* and *chromic acids* it forms a purple- coloured green by *sesquichloride of iron*. (Pe xvii. 1143; Ebermaier, J. pr. Chem. lxii. 2 evi. 382.) With strong *sulphuric acid*, it forms s becomes reddish at first, then green, and ulti throws down a dark blue powder, and renders th small quantity of peroxide of manganese be adder without the aid of heat. An alcoholic solution acquires a dingy red colour; with *ferrie chloride*

Pyroguaiacin dissolves in hot *potash*- and so yield capillary crystals or iridescent laminae, whiel and  $C^{15}H^{21}NaO^2.H^2O$  respectively. The solutio of *silver* a precipitate which soon turns black. (

**GUAIARETIC ACID.**  $C^{20}H^{22}O^4$ .—This of guaiacum, and amounts, according to Hlasiwet (J. Pharm. xxvii. 381), by treating the concentrat baryta-water, precipitating the baryta with sulp to a syrup, dissolving in ether, and leaving the et warty masses, which were converted by sublimat cinnamic or benzoic acid, and very soluble in wat obtained, called by Thierry guaiacic acid, was sition  $C^8H^8O^2$ . By dry distillation, it was re guaiacene:  $C^8H^8O^2 = CO^2 + C^8H^8O$ .

Hlasiwetz (Ann. Ch. Pharm. cxiii. 182), 1



guaiacum with potash and decomposing the resulting potassium-salt with hydrochloric acid, obtained a cream-coloured resin, which crystallised from alcohol in needles of scaly crystals, having a pearly lustre and a faint but agreeable odour of vanilla. This product was regarded by Hlasiwetz as probably identical with Thierry's guaiacic acid.

A more complete investigation of this crystalline acid by Hlasiwetz and Gilm (Ann. Ch. Pharm. cxix. 266; Jahresb. d. Chem. 1861, p. 685) has shown, however, that it has the composition  $C^{20}H^{26}O^4$ . Hence Hlasiwetz now regards it as distinct from Thierry's acid, and designates it as guaiaretic acid.

To prepare guaiaretic acid, Hlasiwetz and Gilm boil pulverised guaiac resin with milk of lime for half an hour, and exhaust the dried insoluble residue in a percolator with hot alcohol; evaporate the alcoholic solution, and dissolve the residue in warm soda-ley of specific gravity 1.3; purify the sodium-salt, which separates on cooling, by recrystallisation from water containing soda; decompose it with hydrochloric acid; and purify the guaiaretic acid thus separated by recrystallisation from strong acetic acid.

Guaiaretic acid forms brittle, concentrically-grouped needles, which are colourless and inodorous, permanent in the air, and melt between  $75^\circ$  and  $80^\circ$  C. It dissolves in alcohol, ether, warm acetic acid, sulphide of carbon, and dilute potash, but not in ammonia, and is precipitated from the potash solution by sal-ammoniac. Its alcoholic solution is coloured grass-green (not blue) by sesquichloride of iron; chlorine-water does not colour it either green or blue; and its aqueous emulsion is not coloured blue by fuming nitric acid. Hence it appears that guaiaretic acid is not the constituent of guaiac resin which produces the blue colour with oxidising agents. (Hlasiwetz and Gilm.)

The solutions of guaiaretic acid turn the plane of polarisation to the left. (Hadelich.) Guaiaretic acid, when quickly heated, distils for the most part unaltered; but by slower distillation, it yields a yellow oily distillate, which is a mixture of guaiacol and pyroguaiacin (p. 948).

**Guaiaretates.**—Guaiaretic acid forms neutral and acid salts. The guaiaretates of the alkali-metals are crystallisable; those of the alkaline earth-metals and heavy metals are amorphous precipitates. The neutral salts are stable only in presence of excess of alkali; when boiled with water, they are converted into acid salts. The *neutral barium-salt*,  $C^{20}H^{24}Ba^2O^4$  (at  $160^\circ$  C.), is formed by decomposing the neutral potassium-salt with chloride of barium. The *neutral potassium-salt*,  $C^{20}H^{24}K^2O^4$  with  $2H^2O$  or  $3H^2O$ , according to the mode of preparation, crystallises from alcohol in scales and gives off its water at  $100^\circ$  C. The *acid potassium-salt*,  $C^{20}H^{22}KO^4.H^2O$ , obtained by boiling the neutral salt with dilute alcohol, or by mixing an alcoholic solution of the acid with carbonate of potassium, and dissolving the precipitate in aqueous alcohol, is a crystalline precipitate which gives off its water at  $120^\circ$  C. The *neutral sodium-salt*,  $C^{20}H^{22}Na^2O^4.2H^2O$ , forms shining crystalline laminae, which become anhydrous at  $120^\circ$  C. The *acid sodium-salt* has the composition  $C^{20}H^{22}NaO^4.H^2O$ .

Hadelich has obtained a *lead-salt* containing  $C^{20}H^{22}Pb^2O^4$ , whence he regards the acid as tetrabasic.

*Bromoguaiaretic acid*,  $C^{20}H^{22}Br^2O^4$ , is obtained in loosely aggregated colourless needles, by dropping bromine into a solution of guaiaretic acid in sulphide of carbon till the liquid acquires a brown colour, evaporating to dryness, washing the residue with cold alcohol, and dissolving it in hot alcohol.

A similar product is obtained with *chlorine*, but it is difficult to purify. *Pentachloride of phosphorus* also forms with guaiaretic acid a tenacious resinous mass difficult to purify.

**GUANIDINE.**  $CH^3N^3 = \begin{matrix} C^{17} \\ H^3 \end{matrix} \{ N^3 \text{ (Carbotriamine), or } \begin{matrix} CN \\ H^3 \end{matrix} \} N^2 \text{ (Cyandiamine).}$

An organic base discovered and investigated by Strecker (Ann. Ch. Pharm. cxviii. 151). It is produced: 1. Together with parabanic acid and small quantities of xanthine, oxaluric acid, and urea, by the action of hypochlorous acid on guanine. When guanine is immersed in hydrochloric acid of specific gravity 1.10, and crystals of chlorate of potassium are gradually added (12 grms. of the chlorate to 20 grms. of guanine in 2 or 3 days) till the base is gradually dissolved, with evolution of gas, the solution then evaporated over the water-bath, and the pasty residue treated with ether-alcohol, a solution is obtained, containing hydrochlorate of guanidine, together with the other products above-mentioned. The parabanic acid crystallises out first; and on diluting the mother-liquor with water, warming it with carbonate of barium, mixing the neutral solution with absolute alcohol, filtering from the resulting precipitate of oxalurate of barium, xanthine-baryta, and chloride of barium, evaporating the filtrate, and treating the residue with absolute alcohol, hydrochlorate of guanidine dissolves, and after removal of the alcohol, may be converted into sulphate by treatment with sulphate of silver. The excess of silver-salt is then removed by adding an exactly equivalent quantity of chloride of barium; the concentrated filtrate is mixed with



absolute alcohol, which soon throws down crystal remaining in solution), and from this salt the base the sulphuric acid with baryta-water, and evaporate.

2. By heating biuret (l. 600) to  $160^{\circ}$ – $170^{\circ}$  C. in small quantity, by boiling that compound with  $= \text{CH}_2\text{N}^2 + \text{CO}^2$ . (Finckh, Ann. Ch. Pharm. c.

Guanidine thus obtained is a crystalline, strong taste. When exposed to the air, it deliquesces and with acids, forming crystalline salts.

*Carbonate of Guanidine*,  $\text{C}^3\text{H}^{12}\text{N}^6\text{O}^3 = \frac{(\text{CO})^3}{(\text{CH}^2\text{N})^3}$

solution of the base in an open vessel, or by decoction of barium, crystallises in quadratic octahedrons,  $\infty\text{P}$ ,  $\text{oP}$ ,  $\infty\text{P}\infty$  and  $\text{P}$ . It is very soluble in water the air, and when heated above  $125^{\circ}$  C. gives off carbonate of ammonium, together with a white diffused yellow residue resembling mellone. The alkaline precipitates with calcium-, barium- and silver-salt.

*Hydrochlorate of Guanidine* crystallises with chloroplatinate,  $\text{CH}^2\text{N}^2.\text{HCl.PtCl}_2$ , crystallises from

*Nitrate of Guanidine* forms prismatic crystals in water, and when heated with nitric acid appear to

*Acid Oxalate of Guanidine*,  $\text{CH}^2\text{N}^2.\text{C}^2\text{H}^2\text{O}^4.\text{H}^2\text{O}$

crystals, sparingly soluble in water. The *sulphate* in water, insoluble in alcohol.

Guanidine is related in composition to several

Carbo- triimine. (Guanidine.)	Methylcarbo- triimine. (Methyluramine.)	Diphenylcarbo- triimine. (Melaniline.)
$\left. \begin{array}{c} \text{C}^1 \\ \text{H}^3 \end{array} \right\} \text{N}^2$	$\left. \begin{array}{c} \text{C}^1 \\ \text{CH}^2 \\ \text{H}^1 \end{array} \right\} \text{N}^2$	$\left. \begin{array}{c} \text{C}^1 \\ (\text{C}^6\text{H}^5)^2 \\ \text{H}^3 \end{array} \right\} \text{N}^2$

**GUANINE.**  $\text{C}^5\text{H}^4\text{N}^4\text{O}$ . (Bodo Unger [Neubauer and Kerner, *ibid.* ci. 318.—Strecker] An organic basic obtained from guano. It exists in the Peruvian, sparingly in the African (Unger) of the excrements of the garden spider, and is found in crab, and in the Bojanian organ of the pond mussel. Ann. Ch. Pharm. lx. 117); also in the pancreas and in the scales of the bleak. (Barreswil, Cor.

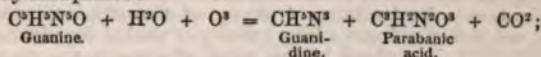
*Preparation from Guano.*—1. Guano is boiled sample exhibits no longer a brown but a green filtered; the filtrate neutralised with hydrochloric acid and guanine, which is completely precipitated hydrochloric acid to extract the latter; the filtrate guanine crystallises out; the crystals purified by guanine precipitated from the aqueous solution product, after washing and drying, amounts to a yellowish guano thus obtained is treated with excess with aid of heat; the liquid is decanted before the dissolved portion, already a purer salt, is collected. In this manner till ammonia precipitates white guanine suspended in water is gradually mixed with milk of lime and the brown solution is strained through a cloth till the liquid becomes colourless. By this means acids and other substances (including nitrate of urea) are removed, while guanine and uric acid remain. The residue is now repeatedly boiled with carbonate of soda are mixed with acetate of sodium, and then with hydrochloric to produce a strong acid reaction. The precipitate is washed with moderately dilute hydrochloric acid. A solution of hydrochlorate of guanine, filtered from hydrochlorate of guanine thus obtained still contains guanine is precipitated from the solution by boiling

solved in hot nitric acid to decompose the uric acid; and from the nitrate of guanine, which crystallises from this solution, the pure base is precipitated by ammonia.

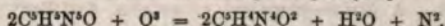
3. According to Neubauer and Kerner, pure guanine is most easily obtained by dissolving the compound of guanine with mercuric chloride in very dilute hydrochloric acid, decomposing the compound with sulphydric acid gas, and precipitating the colourless filtrate with ammonia.

Guanine is a white amorphous powder insoluble in water, alcohol and ether. A hydrate of the base, containing 7.1 per cent. water, is obtained by decomposing the sulphate with a large quantity of water. It resembles the anhydrous base, retains its water at 100° C., but gives up the whole of it at 125°.

Guanine is decomposed by digestion with *hydrochloric acid and chlorate of potassium*, yielding guanidine and parabanic acid, together with smaller quantities of oxaluric acid, xanthine and urea. The formation of guanidine and parabanic acid is represented by the equation:



that of xanthine, which is formed in small quantity only, by



*Nitrous acid* converts guanine into xanthine, the transformation being explained by the equation just given (Strecker).

*Potassium permanganate*, added to a solution of guanine in caustic soda, converts it into oxyguanine,  $\text{C}^{10}\text{H}^4\text{N}^3\text{O}^9$ , with formation of carbonic anhydride, oxalic acid, ammonia, and urea. (Kerner.)

Guanine appears to be sometimes converted in the animal organism into urea: when added to the food of rabbits, it increases the quantity of urea excreted in the urine, which, moreover, does not, under the same circumstances, contain either guanine, uric acid, or hippuric acid: part of the guanine was, however, found in the solid excrements. (Kerner, Ann. Ch. Pharm. ciii. 249.)

*Compounds of Guanine.*—Guanine unites with acids, with alkalis and other metallic oxides, and with metallic salts and chlorides. It dissolves in the stronger acids, but not in formic, acetic, lactic, citric, succinic, or hippuric acid (Neubauer and Kerner). The compounds of guanine with acids are very unstable; they are all decomposed by water, and those which contain volatile acids are likewise decomposed by heat. (Unger.)

*Hydrobromate of Guanine*,  $6(\text{C}^5\text{H}^5\text{N}^3\text{O}.\text{HBr}).7\text{H}^2\text{O}$  (?), crystallises from a hot solution of recently precipitated guanine in hydrobromic acid, in yellowish-white prismatic needles, which effloresce below 100° C., melt at about 180°, and give off their acid at a stronger heat. (Kerner.)

*Hydrochlorate of Guanine*,  $\text{C}^5\text{H}^5\text{N}^3\text{O}.\text{HCl.H}^2\text{O}$ , is obtained in delicate needles by dissolving guanine in strong boiling hydrochloric acid, and leaving the solution to cool. The water of crystallisation is expelled at 100°, and the acid at 200°. Guanine absorbs hydrochloric acid gas and forms a dihydrochlorate,  $\text{C}^5\text{H}^5\text{N}^3\text{O}.2\text{HCl}$ , which gives off half its acid at 100° or in vacuo. (Unger.)

Monohydrochlorate of guanine forms crystalline compounds with the chlorides of cadmium, zinc, mercury, and platinum. The *cadmium-salt*,  $2(\text{C}^5\text{H}^5\text{N}^3\text{O}.\text{HCl}).5\text{CdCl} + \frac{3}{2}\text{aq.}$ , separates on mixing the moderately-concentrated solutions of the component salts, in drusy aggregates of thin white laminae. The *zinc-salt*,  $\text{C}^5\text{H}^5\text{N}^3\text{O}.\text{HCl.ZnCl}.\frac{3}{2}\text{H}^2\text{O}$ , is obtained in large crystals on adding hydrochlorate of guanine to a very strong solution of chloride of zinc. The *mercury-salt*,  $(2\text{C}^5\text{H}^5\text{N}^3\text{O}.\text{HCl}).\text{Hg}^2\text{Cl}^2.\text{H}^2\text{O}$ , is obtained by adding an alcoholic solution of mercuric chloride to strong solution of hydrochlorate of guanine (Neubauer and Kerner). The *platinum-salt*,  $\text{C}^5\text{H}^5\text{N}^3\text{O}.\text{HCl}.2\text{PtCl}_2.2\text{H}^2\text{O}$ , is deposited in orange-yellow crystals on mixing a boiling solution of the hydrochlorate with dichloride of platinum. (Unger.)

*Hydriodate of Guanine*,  $6(\text{C}^5\text{H}^5\text{N}^3\text{O}.\text{HI}).7\text{H}^2\text{O}$  (?), crystallises in the same form as the hydrobromate; it is sparingly soluble in pure water, easily in dilute hydriodic acid. When exposed to air and light, it turns yellow. The mother-liquor yields lemon-yellow concentrically-grouped laminae, containing a larger quantity of iodine. (Neubauer and Kerner.)

*Nitrate of Guanine.* A solution of guanine and boiling nitric acid deposits on cooling capillary interlaced crystals of the neutral nitrate,  $\text{C}^5\text{H}^5\text{N}^3\text{O}.\text{NHO}^3.\frac{3}{2}\text{H}^2\text{O}$ , and shortened prisms of an acid salt,  $\text{C}^5\text{H}^5\text{N}^3\text{O}.2\text{NHO}^3.2\text{H}^2\text{O}$ . Several intermediate nitrates appear also to exist. A *nitrate of mercurousum and guanine* is obtained on mixing the solutions of the compound salts in crystals, which dissolve sparingly in water, and deflagrate, emitting white fumes when heated. (Unger.)

*Oxalate of Guanine*,  $3\text{C}^5\text{H}^5\text{N}^3\text{O}.2\text{C}^2\text{H}^2\text{O}^4$ , separates on mixing a solution of the



hydrochlorate with oxalate of ammonium, in crystals which do not give off any at  $100^{\circ}$  C. (Unger.)

*Phosphate of Guanine* separates in crystals from its solution, but is difficult to obtain pure.

*Sulphate of Guanine*,  $2C^5H^4N^2O \cdot H^2SO^4 \cdot 2H^2O$ , obtained by diluting with water solution of guanine in strong sulphuric acid, forms yellowish needles sometime inch long, which give off their water at  $120^{\circ}$  C. (Unger.) A *sulphate of silver guanine* is obtained on adding nitrate of silver to a very dilute solution of sulphate of guanine, as a bulky translucent precipitate, which shrinks very much in drying, leaves a hard mass of a pale flesh-colour. (Unger.)

*Tartrate of Guanine*,  $3C^5H^4N^2O \cdot 2C^4H^2O^6 \cdot 2H^2O$ , separates from a dilute strongly acid solution, in yellowish radiated nodules, which do not give off any at  $120^{\circ}$  C.

*Compounds of Guanine with Metallic oxides and salts.* Guanine dissolves in aqueous solutions of the caustic fused alkalis. A strong solution of caustic soda, saturated with guanine, and then mixed with a large quantity of alcohol, deposits the compound  $C^5H^4N^2O \cdot NaHO \cdot 2H^2O$ , in confused laminae, which effloresce in the air, and rapidly absorb carbonic acid. Water decomposes them, dissolving the soda and separating guanine (Unger). A *barium-compound of guanine*,  $C^5H^4Ba^2N^2O$ , separates on cooling from a solution of guanine in baryta-water, in needle-shaped prisms, which become opaque when dried over oil of vitriol.

A compound of guanine with *mercuric chloride*,  $C^5H^4N^2O \cdot Hg^2Cl^2 \cdot \frac{1}{2}H^2O$ , is obtained as a white crystalline powder on adding a cold-saturated aqueous solution of mercuric chloride in slight excess to a moderately concentrated solution of guanine in chlorate of guanine. It dissolves readily in acids and in cyanide of potassium (Neubauer and Kerner). A compound of guanine with *nitrate of silver*,  $C^5H^4N^2O \cdot AgNO^3$ , is produced on mixing the solutions of nitrate of silver and nitrate of guanine (Strecker). On adding nitrate of silver to a very dilute solution of *sulphate of guanine*, a bulky translucent precipitate is formed, which shrinks very much in drying. When decomposed by zinc, it yields silver, guanine, and sulphuric acid, but no nitric acid. (Unger.)

**Nitroguanine.** When guanine is dissolved in nitric acid of specific gravity 1.15—at the boiling heat, and the solution, after boiling till it no longer gives a permanent precipitate with ammonia, is left to cool, or evaporated to a syrup and precipitated with water, golden-yellow flocks are obtained, having the composition of *nitro-guanine*,  $C^5H^4(NO^2)N^2O \cdot HNO^2$ , the mother-liquor retaining a portion of the same compound, together with oxalic acid. A slightly alkaline solution of the compound yields orange-yellow precipitates with acetate of lead, and a dingy yellow precipitate with acetate of copper. The silver compound has the formula  $2C^5H^4(NO^2)N^2O \cdot 3Ag^2O$ . (Neubauer and Kerner.)

When to the warm solution of nitrate of nitroguanine, crystals of nitrite of potassium are gradually added till a brisk evolution of nitrous fumes takes place, and the solution is then poured into a large quantity of cold water, lemon-yellow flocks are precipitated, which appear to consist of a mixture of xanthine and nitroxanthine (Strecker.)

**Oxyguanine.**  $C^5H^4N^2O^2$  (?).—When a solution of guanine in caustic soda is treated with a solution of permanganate of potassium till the liquid assumes a reddish-yellow colour, oxyguanine is formed, together with carbonic acid, oxalic acid, ammonia, and urea, and separates from the alkaline solution, on addition of hydrochloric acid, as an amorphous, gelatinous, reddish-white precipitate. It is inodorous and tasteless, insoluble in water, alcohol, and ether, and dissolves but partially when heated with acids: from the nitric acid solution it separates unaltered on evaporation. It dissolves with facility in ammonia, potash, soda, lime-water, and baryta-water, is precipitated from these solutions by carbonic acid; it is, however, slightly soluble in the acid carbonates of the alkali-metals. Its solubility in ammonia distinguishes it from guanine. It does not unite with acids. The ammoniacal solution forms precipitates with acetate of lead and nitrate of silver. The silver-compound appears to contain  $C^5H^4N^2O^2 \cdot Ag^2O$ . (Kerner, Ann. Ch. Pharm. ciii. 249.)

**GUANITE.** Syn. with STRUVITE.

**GUANO.** A substance found on many of the small islands of the Southern Ocean near the coasts of Peru and Bolivia, and on the south-west of Africa. It consists of the excrementitious deposit of sea-birds, and occurs in beds 50 or 60 feet thick, forming a very powerful and valuable manure, for which purpose it has been used for ages in Peru, and within the last twenty years enormous quantities of it have been imported into England and other countries of Europe for agricultural use.

Guano contains a considerable quantity of ammonia, in combination with



oxalic, phosphoric, and carbonic acids; also phosphates and sulphates of earthy and alkaline bases, together with water, organic matter, clay and sand. Its composition is very variable, and it is often adulterated.

The following table will give some idea of the variations in the composition of unadulterated guano (Pelouse et Frémy, *Traité*, 2<sup>me</sup> éd. vi. 595):

Composition of Guano.

	African.			American.		
Combustible organic matter, uric, oxalic, ulmic acid, &c.	39.5	37.0	42.59	11.3	36.5	35.0
Ammonia in the form of carbonate, urate, &c.	9.5	9.5		31.7	8.6	7.5
Fixed alkaline salts, sulphates, phosphates, chlorides, &c.	7.3	6.5	7.08	8.1	6.5	8.2
Phosphates of calcium and magnesium	17.5	18.0	22.39	22.5	20.5	22.5
Oxalate of calcium	. .	. .	. .	2.6		
Sand and earthy matters	1.3	0.5	0.81	1.6	1.5	2.6
Water	25.0	28.5	27.13	22.2	26.0	25.0
	100.1	100.0	100.00	100.0	99.6	100.8

The value of guano depends chiefly on the quantities of ammonia and phosphoric acid which it contains.

For further details on the composition of guano, and for the method of estimating its commercial value, see *Ure's Dictionary of Arts, Manufactures, and Mines*, ii. 413; also *Anderson's Agricultural Chemistry*, Edinburgh, 1853, p. 204.

**GUARINITE.** A silicotitanate of calcium, having the same composition as sphene (*q. v.*), from Monte Somma, where it occurs, together with sphene, in blocks imbedded in tufa, and chiefly consisting of glassy felspar and nephelin. The crystals are dimetric ( $c = 0.3712$ ), exhibiting the faces  $oP$ ,  $P\infty$  (with lateral edge-angle =  $40^\circ 44'$ ),  $2P\infty$ ,  $\infty P\infty$ ,  $\infty P$ ,  $\infty P2$ ,  $\infty P3$ . They are tabular between  $oP$  or  $\infty P\infty$ , and cleave, not very perfectly, parallel to  $\infty P\infty$ . Colour sulphur-yellow. Lustre adamantine. Transparent to translucent. Streak dull. Powder whitish-grey. Fracture irregular. Hardness = 6. Specific gravity = 3.487. The mineral melts before the blow-pipe, without much change of colour; floats in small pieces without alteration, in a bead of phosphorus-salt or borax. Strong hydrochloric acid dissolves it partially, leaving a residue of silica. It gives by analysis 33.64 per cent.  $SiO_2$ , 33.92  $TiO_2$ , 28.011  $CaO$ , with traces of ferric and manganic oxides.

Guarinite likewise occurs (without sphene) in a greyish-violet trachyte, implanted on nephelin; rarely, together with sphene, in the mixture of augite and mica which is so frequent on Somma. (Guiscardi, *Cimento*, vii. 448.)

**GUAYACANITE.** See ENARGITE (p. 488).

**GUIZOTEA OLEIFERA.** The oleaginous seeds of this plant contain 7.02 per cent. water, 43.22 oil, 19.37 albuminous substances, 13.37 sugar, gum, &c., 14.33 cellulose, and 3.48 ash, = 100.08. Nitrogen = 3.10 per cent. (Anderson, *Highland Agr. Soc. J.* new series, No. 69, p. 376.)

**GUM.** *Gomme. Gummi. Pflanzenschleim.* (Gm. xv. 193.—Gerh. ii. 497.)—A vegetable substance which forms a thick glutinous liquid with water, is insoluble in alcohol, and is converted by nitric acid into oxalic and mucic acids. Gums are very abundant in the vegetable kingdom, existing indeed more or less in all kinds of plants. Six kinds of gum are known, viz. *gum-arabic*, *gum Senegal*, *cherry-tree* or *native gum*, *gum of Bassora*, *gum tragacanth*, and *gum of seeds*. The first five, which are called *gums proper*, exude spontaneously from the stems and branches of trees, and sometimes from the fruit; they are more or less soluble in water, both hot and cold. The sixth kind, the *gum of seeds*, also called mucilage, differs from the gums proper, in not being soluble in water, but merely swelling up when boiled with water.

1. *Gum Arabic.* This gum exudes spontaneously from several kinds of acacia (*A. vera*, *A. arabica*, &c.) growing in Arabia and in Egypt. It forms small transparent tears, white when pure, but generally having a yellowish or brownish colour, and cracking in all directions on exposure to the air. It dissolves readily in water, and the solution, acidulated with hydrochloric acid and then mixed with alcohol, deposits white flakes of arabin or arabic acid,  $C^{12}H^{22}O^{11}$  (i. 352), Frémy's gummie

acid. This acid, in combination with lime, magnesia, or the essential part of gum-arabic. When a solution of lead, copper, &c., a precipitate is formed consisting of the lead-compound contains  $C^{12}H^{20}Pb^{2}O^{11}.H^{2}O$ . The lead and earths are soluble in water, but are precipitated by alcohol.

The specific gravity of gum-arabic is 1.355. It contains 17.60 water, the remainder consisting of saline and of calcium, which may be extracted by hot alcohol. It contains potassium, acetate of potassium, and traces of silica.

The aqueous solution of gum-arabic, and of the other gums, are soluble in water, turns the plane of polarisation of pure arabin  $[\alpha] = -36^{\circ}$  (Béchamp). The solution in water, when exposed to the air, and, according to Fermond (*Berthelot's*), after a long time, into a peculiar sugar, which is called Maumené, on the other hand (Compt. rend. xxx. 1850) laevo-rotatory power unaltered for months.

Gum-arabic left for some time in contact with dextrin, and on boiling, into a fermentable dextrin with galactose, the product obtained from milk-sugar (*Chim. org.* ii. 219).

When strong sulphuric acid is covered with a solution of ordinary gum, the gum, after standing for some hours, is converted into metagummic acid; but gum-arabic, previously not converted into metagummic acid under these conditions, pulverised gum-arabic is triturated with strong sulphuric acid after some hours; and on diluting with water, neutralises the solution, and evaporating, sulphogummic acid, a peculiar gum resembling that which is produced from gum-arabic (Bracconnot), and not capable of fermenting.

Gum-arabic, heated with moderately strong nitric acid, yields mucic, saccharic, oxalic and tartaric acids. With phosphoric acid, substitution-products.

Gum, heated in sealed tubes with bromine, yields probably  $C^{12}H^{20}O^{16}Br^4$ , which, when treated with caustic soda, is converted into isodiglycoethyle. Hlasiwetz, *Ann. Ch. Pharm.* cxxii. 96). Gum-arabic, upon being exposed to chlorine, either moist or dry, and very slowly, a quantity of carbonic anhydride being evolved. Gum-arabic, when treated with potassium, and iodine, yields iodoform. (Miller).

Gum solution does not ferment with yeast. Gum-arabic, when treated with chalk and cheese, yields alcohol and a small quantity of lactic acid. Mannite or glycerin. (Berthelot.)

Gum-arabic is much used in medicine to form emulsions, in numerous processes in the arts. It is added to the tannate of iron, which would otherwise separate from the solution for similar purpose. Large quantities of it are also used in silk, for thickening colours, &c.

2. *Gum Senegal*, obtained from a species of acacia, is very much like gum-arabic. It occurs in commerce in the size of a partridge's egg, or sometimes larger. Its specific gravity, 1.436. It contains 81.10 per cent. arabin, and 18.90 saline matters. It forms a somewhat stronger mucilage than gum-arabic, and is used in calico-printing for thickening the colours and for the same purposes.

3. *Cherry-tree gum*, which exudes from trees, is found in commerce in large shining reddish lumps, often containing a thick mucilage with water, but is only partially soluble in water. It contains arabin, and the insoluble portion contains a substance of peculiar character, which, according to Frémy, is a compound of gum-arabic and oxalic acid. Cherry-tree gum contains 52.1 per cent. arabin, 34.1 per cent. water, and 13.8 per cent. matter. It is used by hatters for smoothing the nap of hats.

*Metagummic acid*, the organic constituent of metagummic acid, is obtained from gum-arabic by leaving a syrupy solution of that substance in water, (see above), by heating the solid gum for some time in water, and adding oxalic acid (Frémy). When prepared by the first method, it contains 60.2 C, 6.02 H and 53.02 O, agreeing approximately with the formula  $C^{12}H^{20}O^{16}$ , and is not altered by boiling.



with *alkaline water* or with a small quantity of *lime*, it is converted into a salt of arabic acid. In like manner, natural cerasin, and metagummate of calcium obtained by heating gum-arabic, are dissolved by boiling with water. Natural cerasin likewise dissolves more easily when boiled with water, after addition of an alkaline carbonate, and with separation of carbonate of calcium (Frémy). Cerasin boiled with *nitric acid* of specific gravity 1.139 yields as much mucic acid as gum-arabic. (Guérin-Varry.)

4. *Gum of Bassora*, which appears to be the produce of a cactus, is white or honey-coloured, mealy and silvery on the surface, and in the form of somewhat flattened and elongated masses. It is insipid, and crackles between the teeth. In water it swells up to a transparent jelly, but only a small portion dissolves. The soluble portion contains arabin, amounting to about 1 per cent. of the gum; the insoluble portion contains bassorin (i. 519); it dissolves with the aid of heat in potash and in weak acids.

5. *Gum Tragacanth* or *Adragant* exudes from the *Astragalus verus*, a tree growing in Armenia and the north of Persia. It is met with in contorted or vermiculated threads, white or yellow, and opaque; specific gravity 1.384. It swells up in water and dissolves to about one-half. The soluble portion contains arabin; the insoluble portion contains grains of starch, and is turned blue by tincture of iodine. It is dissolved almost completely by dilute sulphuric, hydrochloric and oxalic acids at a temperature of 90° or 100° C. The filtered liquid treated with alcohol deposits flocks of arabin, and a considerable quantity of glucose remains in solution. Gum tragacanth dissolves almost entirely in water when boiled with it for some time. It contains 53.3 per cent. arabin, 33.3 bassorin and starch, 11.0 water, and 2 to 3 saline matters. It is used in medicine and in calico-printing, also by shoemakers.

6. *Gum of seeds and roots, or Mucilage*.—This substance appears to be a universally diffused constituent of plants, and is especially abundant in marsh-mallow root, in the tubers of various species of orchis (*Salep mucilage*), the seeds of *Plantago psyllium*, linseed, the seeds of quinces, and of various species of *Salvia* and other *Labiatae*, in the bark and leaves of the lime and elm, and in certain algae, especially *Sphaerococcus crispus*, of which it forms nearly the entire substance, and *Fucus saccharinus*. By steeping either of these seeds, roots, &c., in hot water, the mucilage is obtained in the form of a thick jelly, consisting of minute cells enclosing a soluble substance, and swollen by absorption of water. On digesting it with dilute sulphuric acid at 80° to 100° C., it dissolves completely, and the solution contains glucose. To obtain the soluble part of mucilage, linseed is shaken up with cold acidulated water, the liquid filtered and heated to coagulate albumin, then concentrated and precipitated by alcohol. The substance thus obtained is less transparent and brittle than ordinary gum. It is soluble in cold water, but the solution is not so clear or so ductile as that of gum. According to Nägeli and Cramer (*Pharm. Centr.* 1855, p. 426), it swells up when water is poured upon it, but does not form a true solution. It is insoluble in alcohol, and is precipitated from its aqueous solution, or infusion, by *tincture of galls*.

The aqueous solution of the mucilage of *Plantago psyllium* is not altered by dilute acids, but quince-mucilage is coagulated by acids, alkalis, and many salts. Mucilage boiled with *nitric acid* yields oxalic acid, and, according to older authorities, likewise mucic acid. According to Nägeli and Cramer, quince-mucilage yields, with nitric acid, nothing but oxalic acid. The ash of mucilage contains carbonate and phosphate of calcium, sometimes, also, magnesia, iron, and potash.

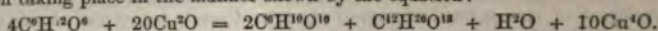
7. *Artificial gums*.—*a. British Gum, Artificial Gum, or Dextrin*, produced by the torrefaction of starch, resembles gum in forming a viscid solution with water; but this solution turns the plane of polarisation of a ray of light to the right, whereas the solutions of all natural gums turn it to the left. (See Dextrin.)

*b. Gum from Sugar, C<sup>12</sup>H<sup>20</sup>O<sup>12</sup>*.—This gum is produced, together with Reichardt's gummic acid, in the oxidation of glucose by cupric salts. It is precipitated by basic acetate of lead (p. 956) and freed from lead by sulphydric acid and from adhering gummic acid by evaporation (the gummic acid being then carbonised) and filtration, and then precipitated by alcohol. It obstinately retains a portion of the alkali used in the preparation.—It is very hygroscopic, nearly tasteless, and easily soluble in water, forming a solution which may be used for the same purposes as ordinary gum. Nitric acid converts it into oxalic acid. By boiling with sulphuric acid, it is reconverted into a sugar which reduces cupric salts. With cupric acetate and excess of alkali, the gum forms a transparent blue liquid, which when boiled deposits a greenish precipitate not altered by prolonged boiling. (Reichardt.)

**GUMMIC ACID.** Frémy's name for the organic acid (Neubauer's *arabin* or *arabic acid*) which in combination with lime (and according to Neubauer, also with magnesia and potash) constitutes gum arabic. Frémy regards the relation between gummic and metagummic acid (p. 954) as similar to that which exists between soluble pectin-substances and insoluble pectose.



The same name is applied by Reichardt (Ann. Ch. Pharm. cxxvii. 300) to crystalline acid,  $C^6H^{10}O^{10}$ , which he finds to be produced, together with a peculiar kind of gum, in the oxidation of glucose by cupric oxide in alkaline solution (p. 860) the reaction taking place in the manner shown by the equation:



To prepare gummic acid, cupric acetate mixed with a slight excess of alkali is heated to about  $60^\circ C$ . and glucose added till the reduction is complete, small portions of alkali being added from time to time, to replace that which has been neutralised by the gummic acid formed. The filtered liquid is then neutralised with acetic acid; the gummic acid is precipitated by sulphydric acid or chloride of barium, and the gum from the filtrate by basic acetate of lead.

Gummic acid separated from the lead-precipitate by sulphydric acid or from the barium precipitate by sulphuric acid, crystallises by evaporation, first at a gentle heat afterwards over chloride of calcium, in rhombic prisms having a strong acid taste like that of citric or tartaric acid. At  $100^\circ C$ . it does not give off water, but begins to emit acid vapours; it turns brown at  $130^\circ$ , and melts with intumescence at  $150^\circ$ , giving off water in continually increasing proportion together with acid vapours. Of the residue left after heating the acid to  $210^\circ$ , only a small portion is soluble in water.

The gummates of the alkali-metals are soluble in water; the other salts sparingly soluble. To the barium- and silver-salts, Reichardt assigns the formula  $2MO.C^6H^5O^6.HO$ , and to the lead-salt,  $3PbO.C^6H^5O^6.HO$ .

**GUM-RESINS.** When incisions are made in the stems, branches, or roots of some vegetables, there exudes a milky juice, which gradually hardens in the air, and seems to be formed of resin and essential oil, kept in suspension by water, often loaded with gum and several other vegetable matters. To this solidified juice the name gum-resin is given,—an improper one, since it gives a false notion of the body it represents. All the gum-resins are solid, denser than water, opaque and brittle; the greater number have an acrid taste and a strong smell. Their colour is very variable. Water dissolves them in part, and so does alcohol. The aqueous solution becomes transparent with difficulty. When water is poured into the alcoholic solution, it becomes immediately turbid, the resinous matter separating in a state of extreme division, and giving to the liquor a milky aspect. The principal gum-resins are frankincense, scammony, asafetida, aloes, euphorbium, galbanum, myrrh, olibanum, opoponax, gum-ammoniac and gamboge. U.

**GUM-LAC.** See LAC.

**GUN-COTTON.** See PYROXYLIN.

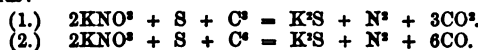
**GUNPOWDER.** The invention of gunpowder, which has been ascribed to popular tradition, in Germany to Berthold Schwartz, a Benedictine monk who lived about the beginning of the fourteenth century, and in this country to Roger Bacon in the latter part of the thirteenth century, has been found by recent investigations to date from a much earlier time. Rockets and other incendiary projectiles appear to have been known to the Chinese at least two centuries before the Christian era; and the Greek historians relate that Alexander, in his expedition into India, was deterred from attacking the Oxydracæ, a tribe dwelling between the Hyphasis and the Ganges, because they were under the care of the gods, and overthrew their enemies with thunder and lightning, which they shot from their walls. We know with certainty that gunpowder was used in the eighth century of the Christian era: for the work of Marcus Græcicus, entitled "*Liber ignium ad comburendos hostes*," contains exact directions for making a rocket and preparing the powder for charging it, and even recommends that the charcoal should be prepared from willow-wood, while modern experience has shown to be one of the best woods for the purpose. Roger Bacon, writing in the thirteenth century, speaks of gunpowder as a composition well known in all countries for making squibs and other fireworks.

The rocket appears to have been for a long time the only form of incendiary projectile used in war. The first mention of cannon is by an Arabian author, who speaks of them as having been used by the King of Granada at the siege of Baza in 1323. An authentic record of the republic of Florence shows that fire-arms were known in that city in 1325; and in France the public accounts of expenditure from 1335 to 1345 show that fire-arms were then employed in war. Field artillery appears to have been first used by the English at the battle of Cressy in 1346. (*Encyclopædia Britannica*.—*Traité de Chimie générale par Pelouze et Frémy*, 3<sup>me</sup> éd. ii. 261.)

*Composition of Gunpowder, and of the products formed by its combustion.* Gunpowder, as everybody knows, is a mixture of nitre, sulphur, and charcoal, and its explosive power depends upon its property of burning rapidly and with great rise of temperature and evolving by its combustion a quantity of gas which occupies more than 1000 times

the volume of the original powder. The quantity and chemical composition of the gases thus evolved depend upon the proportions in which the nitre, sulphur, and charcoal are mixed.

It was formerly supposed that, in the combustion of gunpowder, the whole of the nitrogen was set free, and that the whole of the oxygen of the nitre entered into combination with the charcoal, forming carbonic anhydride, carbonic oxide, or a mixture of the two, while the potassium of the nitre combined with the sulphur, forming sulphide of potassium, thus:



Powder composed according to the first of these formulæ contains 74·9 per cent. nitre, 11·8 sulphur, 13·3 charcoal; and yields, according to theory, 48·9 per cent. by weight of carbonic anhydride, 10·3 nitrogen, and 40·7 sulphide of potassium. A cubic inch of this powder\* should yield 74·6 cubic inches nitrogen, and 22·13 carbonic anhydride, or 296 cubic inches of gas in all.

The second kind of powder contains by weight 65·4 per cent. nitre, 10·4 sulphur, and 24·2 charcoal, and should yield, according to the second of the above equations, 54·9 per cent. by weight of carbonic oxide, 9·1 nitrogen, and 36·0 sulphide of potassium, or 1 volume of it should yield 66 vols. nitrogen and 391 vols. carbonic oxide = 457 vols. gas.

It appears, then, that the second kind of powder is capable of yielding  $1\frac{1}{2}$  times as great a volume of gas at the same pressure and temperature; but on the other hand, carbon, in burning to carbonic anhydride, evolves a far greater quantity of heat than in burning only to carbonic oxide, and the greater expansion of the gases thence resulting more than compensates for the smaller quantity of gas originally produced. Moreover, the second kind of powder burns so slowly, that the combustion is not complete by the time the ball issues from the gun, so that part of the projectile force is lost.

The actual products of the combustion of gunpowder are in reality much more complicated than they appear to be from the preceding theoretical considerations; nevertheless experience has shown that the best kinds of powder for fire-arms, both large and small, are composed very nearly in the proportions indicated by the first of the formulæ above given, as may be seen by comparing the percentage composition of the various kinds of powder for fire-arms given in the following table, with the theoretical composition of the powder No. 1.

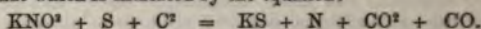
*Composition of Gunpowder.*

Description of Powder.	Charcoal.	Sulphur.	Nitre.	Authority.
Swedish war powder . . .	9·0	16·0	75·0	Meyer
Wurtemberg musket powder . .	10·6	14·8	74·6	"
Hessian artillery powder . . .	10·7	15·1	74·2	"
" musket powder . . .	10·7	15·6	73·7	"
Hanoverian war powder . . .	10·8	18·0	71·2	"
Mailand " . . .	11·9	11·9	76·2	"
Grenelle powder . . .	11·9	11·9	76·2	"
Italian war powder . . .	12·0	12·0	76·0	Prechtl
Dartford powder . . .	12·6	7·7	79·7	Meyer
Curtis and Harvey's powder . .	12·7	9·2	78·1	"
Wurtemberg war powder . . .	12·3	12·5	74·6	Linck
Austrian musket powder . . .	13·1	11·3	75·6	"
Hessian war powder . . .	13·3	13·4	73·3	"
French sporting powder from Angoulême and Le Bouchet . .	13·5	9·6	76·9	Prechtl
English, from Waltham Abbey . .	13·7	10·1	76·2	Ure
Bernese powder . . .	14·0	10·0	76·0	Meyer
Miethen powder (1848) . . .	15·9	9·0	75·1	"
French round powder from Essonne . . .	16·0	10·0	74·0	Prechtl
Dutch artillery powder . . .	16·0	13·9	69·8	Meyer
Russian " . . .	17·7	11·7	70·6	"
Italian sporting powder . . .	18·2	8·6	73·2	Prechtl
Powder from Champy . . .	18·9	4·8	76·3	Meyer
Chinese powder . . .	23·1	15·4	61·5	Prechtl

\* According to Gay-Lussac, the weight of a given volume of gunpowder is 0·9 that of an equal bulk of water.

In all these kinds of powder, excepting the Chinese, which approaches nearest to No. 2 (p. 957), the proportions of the ingredients are nearly the same, the variations arising chiefly from the different degrees of purity of the materials used; some the proportion of charcoal is increased, and that of sulphur diminished, to allow for the smaller percentage of carbon in the charcoal employed; in others the percentage of nitre is somewhat increased, probably to obtain a more rapidly burning powder.

Blasting powder usually contains a larger proportion of sulphur, which is a cheaper material than charcoal, and may be used in excess in the composition of this powder but if present in large quantity in powder for fire-arms, would corrode the metal. The composition of French blasting powder, and of its products of combustion, is approximately that which is indicated by the equation:



100 pts. of this powder contain 64.3 pts. nitre, 20.4 sulphur, and 14.7 charcoal, and should yield by combustion 39.0 pts. by weight of disulphide of potassium, 9.9 N, 31.2 carbonic anhydride, and 19.9 carbonic oxide.

The actual products of the combustion of gunpowder are, however, as already observed, much more complicated than the preceding theory would indicate; notwithstanding the near agreement of the composition of the best kinds of powder with that pointed out by theory, the equations above given cannot be taken as the real representation of the chemical change which takes place, inasmuch as the residue of the combustion is found to consist mainly of sulphate and carbonate of potassium, with only a small quantity of sulphide. When powder burns in contact with the air, it might be supposed that the sulphate of potassium is formed from the sulphide by atmospheric oxidation; but the same result is obtained in burning powder in a close vessel or even in a vacuum, whence it follows that the sulphate of potassium is a direct product of the combustion of the powder independently of atmospheric oxidation.

Gay-Lussac and Chevreul, by burning gunpowder in a copper tube, obtained a gaseous mixture containing in 100 pts. 45.4 pts.  $\text{CO}_2$ , 37.5 N, 8.1  $\text{NO}_2$ , 0.6 carburetted hydrogen, and 8.3 of a peculiar gas containing carbon, hydrogen, and oxygen. In another experiment, they obtained 53 per cent.  $\text{CO}_2$ , 42 N, and 5 CO. The solid residue was found to contain sulphate, carbonate, and the higher sulphides of potassium, as well as the protosulphide.

More elaborate investigations of the products of combustion of gunpowder have been made of late years by A. Vogel, jun. (Dingl. pol. J. cxxxvi. 156), by Bunsen and Schischkoff (Pogg. Ann. cii. 321; Wagner's Jahresh. 1857, p. 131; 1858, p. 158); by Linck (Ann. Ch. Pharm. cix. 53); and by Karolyi (Phil. Mag. [xxvi. 272). The experiments of Bunsen and Schischkoff were made with sporting powder; those of Linck with Wurtemberg war-powder: those of Karolyi with Austrian war-powder. The following table exhibits a comparative view of the results of the experiments:—

		Bunsen and Schischkoff.	Linck.	Karolyi.	
		Sporting powder.	War powder.	Small-arm powder.	Ordnance powder.
Charcoal	Nitre . . . . .	78.99	74.66	77.15	73.78
	Sulphur . . . . .	9.84	12.49	8.63	12.80
	Carbon . . . . .	7.69	12.31	11.78	10.88
	Hydrogen . . . . .	0.41	} 0.54 {	0.42	0.38
	Oxygen . . . . .	3.07		1.79	1.82
	Ash . . . . .	..	..	0.28	0.31
		100.00	100.00	100.05	99.97

*Gaseous Products of Combustion by Volume.*

Nitrogen . . . . .	41.12	34.68	35.33	37.58
Carbonic anhydride . . . . .	52.67	52.14	48.90	42.74
Carbonic oxide . . . . .	3.88	4.33	5.18	10.19
Hydrogen . . . . .	1.21	1.63	6.90	5.93
Sulphydic acid . . . . .	0.60	7.18	0.67	0.86
Oxygen . . . . .	0.52	0.04		
Marsh gas . . . . .			3.02	2.70
	100.00	100.00	100.00	100.00



*Total Products of Combustion by Weight.*

	Bunsen and Schischkoff.	Linck.	Karolyi.	
	<i>Sporting powder.</i>	<i>War powder.</i>	<i>Small-arm powder.</i>	<i>Ordnance powder.</i>
Sulphate of potassium . . . . .	42.27	29.01	36.17	36.95
Carbonate . . . . .	12.64	15.43	20.78	19.40
Hyposulphite . . . . .	3.27	9.63	1.77	2.85
Sulphide . . . . .	2.13	3.75	. .	0.11
Sulphocyanate . . . . .	0.30	1.16		
Nitrate . . . . .	3.72	1.20		
Charcoal . . . . .	0.73	1.84	2.60	2.57
Sulphur . . . . .	0.14	0.31	1.16	4.69
Sesquicarbonate of ammonium . . . . .	2.86	2.05	2.66	2.68
Nitrogen . . . . .	9.98	9.55	10.06	9.77
Carbonic anhydride . . . . .	20.12	22.47	21.79	17.39
Carbonic oxide . . . . .	0.94	1.18	1.47	2.64
Hydrogen . . . . .	0.02	0.03	0.14	0.11
Sulphydic acid . . . . .	0.18	2.38	0.23	0.27
Oxygen . . . . .	0.14	0.01		
Marsh gas . . . . .	. .	. .	0.49	0.40
Loss . . . . .	0.56	. .	0.68	0.17
	100.00	100.00	100.00	100.00
Quantity of gas (in cubic centime- tres) for a gramme of powder . . }	193.10	218.35	226.59	200.91

Bunsen and Schischkoff find that the smoke of gunpowder has nearly the same composition as the solid residue of the combustion, consisting mainly of sulphate, carbonate, and hyposulphite of potassium.

The heat produced by the combustion of gunpowder has been variously estimated by different observers. Bunsen and Schischkoff found that one gramme of sporting powder evolved, in burning, a quantity of heat sufficient to raise the temperature of an equal weight of water 643.92° C. This number, however, must be diminished by the amount of heat due to the further combustion of the inflammable gases present by the air mechanically enclosed within the powder. This correction reduces the amount of heat due to the actual combustion of the powder to 619.5° C.; and this number divided by the sum of the specific heats of the products of combustion (estimated by B. and S. as = 0.207) gives 2993° C. for the temperature of the flame produced by the combustion of gunpowder. If the powder is burnt in a confined space, so that the gases cannot expand, the temperature of the flame will be considerably higher, equal in fact to the quotient obtained by dividing the heat of combustion by the specific heat of the products referred to a constant volume, that is to say,  $\frac{619.5}{0.185} = 3340^{\circ} \text{C.}$

The maximum pressure exerted by the gases, at the first instant of evolution, on the inner surface of the gun, and on the projectile, is estimated by Bunsen and Schischkoff at 4374 atmospheres. Former experimenters had estimated it at much higher amounts, but the data on which their calculations were founded do not appear to be very trustworthy. The greatest mechanical effect or *theoretical working effect* of the powder examined by Bunsen and Schischkoff is estimated by them at 67,149 metre-kilogrammes\* for a kilogramme of powder.

For descriptions of the machinery and processes used in the manufacture of gunpowder see *Richardson and Watts's Chemical Technology*, vol. i. pt. iv.—*Abel and Bloxam's Handbook of Chemistry*, London, 1854, p. 239.—*Üre's Dictionary of Arts, Manufactures, and Mines*, ii. 429.—*Regnault, Cours de Chimie élémentaire*, ii. 291.—*Pelouze et Frémy, Traité de Chimie générale*, 3me éd. ii. 293.

*Analysis of Gunpowder.*—1. *Determination of Moisture.*—A known weight of the powder is either placed for several days in a vacuum over oil of vitriol, or it is placed in a U-tube kept at a temperature of 60° or 70° C. and exposed to a current of dry air. In either case the loss of weight of the powder gives the quantity of moisture contained in it.

2. *Determination of the Nitre.*—10 grms. of the dry powder are digested in hot water, and the undissolved residue, consisting of sulphur and charcoal, is collected on a small filter previously dried and weighed, then washed, dried, together with the filter, at a moderate heat, and weighed. The total weight, diminished by that of the filter, gives the sum of the weights of the sulphur and carbon, which, deducted from the original weight of the powder, gives the nitre. The latter may also be determined directly by

\* A metre-kilogramme is the force represented by the fall of a kilogramme weight through the height of 1 metre.

evaporating the aqueous solution, together with the wash-waters, and drying the residue in a small porcelain capsule at 149° C.

3. *Determination of the Sulphur and Charcoal.*—A weighed portion of the dry residue of charcoal and sulphur obtained as above is introduced into a small flask, and digested with a mixture of sulphide of carbon and ether, which dissolves the sulphur and leaves the charcoal. The latter is collected on a small tared filter, washed with the mixture of sulphide of carbon and ether, then dried and weighed. The weight of the sulphur is known by difference; or it may be determined directly by evaporating the solution, and weighing the residue.

Some analysts dissolve out the sulphur by means of a solution of sulphide or hyposulphite of sodium; but this method is objectionable, because these liquids likewise attack the charcoal, forming a peculiar acid called *ulmic acid*.

The charcoal in gunpowder is not pure carbon, but contains also hydrogen and oxygen, varying in quantity according to the degree to which the carbonisation has been carried. Its composition has a great influence on the quality of the powder, and must therefore be determined when a complete analysis is desired. The analysis of the charcoal is made by combustion with oxide of copper, as described under ANALYSIS, ORGANIC (i. 232).

The quantity of sulphur in gunpowder may also be determined by operating directly on the powder itself. For this purpose, 10 grms. of the dry powder are digested in a small quantity of hot water, nitric acid is added, the whole heated to boiling, and chlorate of potassium added by small quantities. The sulphur then dissolves in the form of sulphuric acid, and may be precipitated from the filtrate by chloride of barium. The precipitate of sulphate of barium is collected and washed, with the precautions indicated at page 503, vol i., then dried and weighed, and the amount of sulphur thence determined.

Another method of determining the sulphur is to mix a known weight of the dry powder with an equal weight of nitre and 4 or 5 times the same weight of chloride of sodium, and throw the mixture by small portions into a red-hot platinum crucible. Deflagration then takes place slowly, without projection of the mixture. When it is ended, the fused mass is taken up with water, the liquid is supersaturated with hydrochloric acid, and the sulphuric acid is precipitated by chloride of barium.

It is sometimes required to determine merely the percentage of nitre contained in a sample of gunpowder. This is easily done by treating 50 grammes of the powder with 200 grammes of hot water, and filtering the liquid into a glass cylinder having a mark indicating the capacity of 500 cubic centimetres. The residue on the filter is washed with water till the filtered liquid just fills the cylinder up to the mark. The liquid is then cooled to 15° C., and a small quantity of water is added to make up for the contraction caused by cooling. It is then well stirred to render it homogeneous, and a small hydrometer is immersed in it, graduated in such a manner that the degree to which it is immersed indicates immediately the number of hundredth parts of nitrate of potassium contained in the 50 grammes of powder. By this method the proportion of nitre may be easily estimated within 0.3 per cent. (Regnault.)

**GURHOFITE**, or *Gurhofian*.—A variety of dolomite found at Phillipstown, New York. It has a semi-opaline appearance, and a fracture nearly like that of porcelain.

**GUROLITE**. See **GYROLITE**.

**GUTTA PERCHA**. A substance resembling caoutchouc, obtained from the *Isanarda Percha* (Hooker) or *Is. Gutta*, a large tree of the sapotaceous order, growing in the peninsula of Malacca, Borneo, and many of the other islands of the Indian Archipelago, also, according to Bleekrode (Rép. Chim. app. i. 403) from *Sapota Muelleri*. It exudes from incisions in the bark, and is usually procured by the wasteful process of cutting down the trees, ringing the bark at distances of 12 or 18 inches apart, and placing a cocoa-nut shell, spathe of a palm, or some similar receptacle, under the trunk, to receive the milky sap which exudes from the incisions. The juice is afterwards inspissated by boiling.

The crude gutta percha imported into Europe is prepared for manufacturing purposes by rasping it in cold water, whereby it is freed from the greater part of the soluble salts, earthy matters, and extraneous organic substances which it contains, and washed with tepid water in a series of large basins. The residue is then heated for some time to 110° C. (230° F.) to reduce it to a single mass, and expel the last traces of water, which would otherwise remain between the particles of the gutta percha and diminish its coherence.

Another mode of purification is to dissolve the crude gutta percha in sulphide of carbon, filter the brown turbid solution under a bell-jar, and leave the limpid colourless filtrate to evaporate in the air in shallow porcelain dishes or on plates of glass. On



pouring cold water on the dry residue, the films separate from the glass or porcelain after a few minutes, and may be lifted off without breaking. (Payen.)

Purified gutta percha has a brownish red colour and a density of 0.979. It becomes electrical by friction, and is a very slow conductor of electricity. Hence it is much used for forming insulating supports in electrical apparatus, and for coating telegraph wires which are to be immersed in water. At the ordinary temperature of our climate, it possesses considerable tenacity, about equal to that of strong leather, and somewhat less flexibility. At about  $48^{\circ}$  C. ( $115^{\circ}$  F.) it softens and becomes pasty, though still very tenacious. Between  $42^{\circ}$  and  $60^{\circ}$  C. ( $103^{\circ}$  and  $104^{\circ}$  F.) it may easily be spread out into sheets or drawn into threads or tubes. Its suppleness and ductility diminish as the temperature lowers, and it does not possess, at any temperature, the elastic extensibility of caoutchouc. When softened by heat, it may be worked by pressure into any required shape, and will take the finest impressions of a mould; hence it is much used for ornamental mouldings of picture frames, &c.

Gutta percha is remarkably porous; a thin film of it obtained by leaving a drop of its solution in sulphide of carbon to evaporate spontaneously on a plate of glass, appears, when examined by the microscope, to be full of minute pores, like a sieve. This porous structure may be changed by traction into a fibrous structure, the gutta percha being capable of extending in this manner to double its original length; it then possesses little further extensibility, but will support without breaking a force equal to the double of that which produced the extension.

Gutta percha is insoluble in water, sparingly soluble in anhydrous alcohol and anhydrous ether. It dissolves in small quantity in boiling olive oil, and is deposited from the solution on cooling. Benzene, sulphide of carbon, chloroform, and oil of turpentine dissolve it easily with the aid of heat. It resists the action of alkaline solutions, of hydrochloric acid, and of hydrofluoric acid: bottles made of gutta percha form very convenient receptacles for hydrofluoric acid. It is carbonised by strong sulphuric acid, and converted into a yellow resin by nitric acid. By dry distillation it yields very inflammable oils.

According to Payen (Compt. rend. xxxv. 109), gutta percha purified by solution in sulphide of carbon, as above described, is a mixture of three proximate principles; viz. —1. A portion insoluble in alcohol, whether cold or boiling, and amounting to 75–82 per cent. of the whole. This is called by Payen pure gutta.—2. A crystalline substance called alban, insoluble in cold, but soluble in boiling alcohol; this has been already described (i. 64), it amounts to 19–14 per cent. of the gutta percha.—3. A yellow resinous substance called fluavil (ii. 669) soluble in cold alcohol, and amounting to 6–4 per cent. of the whole. According to Payen, these three substances are isomeric, their composition being expressed by the formula  $C^9H^{14}$ . Payen's pure gutta is white, opaque, elastic; softens and becomes adhesive at  $50^{\circ}$  C.; melts at about  $100^{\circ}$ ; dissolves in benzene when heated, in sulphide of carbon at ordinary temperatures, but is insoluble in alcohol and in ether.

From the experiments of Oudemans (Rép. Chim. app. i. 455), and of v. Baumhauer (J. pr. Chem. lxxviii. 277), it appears however that pure gutta is a hydrocarbon isomeric with oil of turpentine,  $C^{10}H^{16}$ , and that alban and fluavil are formed from it by oxidation,—fluavil being  $(C^{10}H^{16})^2O$  and alban  $C^{10}H^{16}O$ ,—probably together with a whole series of other products of oxidation, including formic acid. This oxidation appears to take place during the extraction of the gutta percha from the trees, and if it could be prevented, there is no doubt that pure gutta would be at once obtained. (Bleekrode.)

Baumhauer prepares pure gutta by exhausting gutta percha with water and hydrochloric acid, and treating the residue with boiling ether (which dissolves everything excepting a few black flocks), leaving the filtrate to cool, pressing the substance which separates, and repeating the treatment till the ethereal liquid retains nothing in solution after cooling.

Pure gutta thus prepared is perfectly white when reduced to fine powder; cakes together and becomes transparent at  $100^{\circ}$  C., becoming somewhat turbid on cooling, and more so after some time; at  $150^{\circ}$  it begins to melt and is converted into a tenacious mass; at  $180^{\circ}$  an oily liquid begins to distil over; at  $210^{\circ}$  the mass becomes filled with vapour-bubbles, and at  $280^{\circ}$  it froths strongly. Gutta is strongly attacked by ozonised oxygen; also by strong hydrochloric acid, with which it appears to form two compounds containing chlorine. It is insoluble in cold ether, but becomes soluble after exposure to the air.

The view just given of the constitution of gutta percha is confirmed by the results of its dry distillation. Greville Williams (Chem. Soc. J. xv. 124) finds that gutta is decomposed by dry distillation, essentially in the same manner as caoutchouc, being resolved, for the most part, into the polymeric hydrocarbons, isoprene,  $C^5H^8$ , and caoutchin,  $C^9H^{16}$ , and heveene, which is probably also polymeric with the other two



The caoutchouin forms about 20, the isoprene about 5 per cent. of the crude distillate. The distillate also contains a small quantity of water, which, instead of being alkaline as with caoutchouc, is strongly acid, and contains a volatile acid, apparently one of the lower members of the series  $C^xH^{2x}O^2$ . On neutralising the acid liquid with potash or soda, the odour of a volatile base becomes perceptible.

**Alterations of Gutta Percha.** Both the ordinary substance and the pure gutta obtained as above, experience, when exposed to the air, especially at a temperature of  $25^\circ$  to  $30^\circ$  C. ( $77^\circ$  to  $86^\circ$  F.) and in thin sheets or threads, a peculiar alteration which takes place with various degrees of rapidity, and completely deprives the material of its flexibility, tenacity, and extensibility, thereby rendering it quite useless for industrial purposes; at the same time a peculiar pungent odour is evolved, which communicates itself to water or other liquids kept in vessels made of the gutta percha (Payen). This alteration is especially liable to occur in tropical climates, an instance of which was experienced in the construction of the East Indian telegraphs. Enormous quantities of gutta percha employed for this purpose became in a comparatively short time entirely useless, involving a loss of thousands of pounds. This altered gutta percha was submitted for examination to Dr. Hofmann (Chem. Soc. Qu. J. xiii. 87), who found that the change was due to oxidation. The altered gutta percha was a brown very brittle mass, from which cold alcohol extracted a brittle substance containing, on the average, 62.8 per cent. carbon, 9.3 hydrogen, and 27.9 oxygen. From the residue of this operation, boiling alcohol extracted a substance of similar physical character, containing on the average 67.7 per cent. carbon, 10.1 hydrogen, and 22.2 oxygen. The residue, insoluble both in cold and in boiling alcohol, was unchanged gutta percha, which yielded by analysis 88.1 per cent. carbon and 12.5 hydrogen. On the oxidation of gutta percha, see also Adriani (Chem. News, ii. 227, 289, 313; Jahresh. 1860, p. 496).

Respecting the manufacture and uses of gutta percha, see *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 433; also Payen, *Précis de Chimie industrielle*, 4me. éd. (1859) i. 184.

**GUYAQUILLITE.**  $C^{20}H^{40}O^4$ .—A fossil resin, said to form an extensive deposit near Guayaquil in South America. It yields easily to the knife and may be rubbed to powder. Specific gravity 1.092. Colour pale yellow. Lustre not resinous, or imperfectly so. Slightly soluble in water and largely in alcohol, forming an intensely bitter yellow solution. Begins to melt at  $157^\circ$  F., but does not flow easily till heated to  $212^\circ$  F. Becomes viscid as it cools, and may be drawn out into fine threads. Dissolves in cold sulphuric acid, with dark reddish brown colour. A few drops of ammonia added to the alcoholic solution darken the colour and finally change it to a brownish red. Contains 76.665 per cent. C, 8.174 H, and 15.161 O. (Johnston, Phil. Mag. xiii. 329; Dana, ii. 468.)

**GYMNITE.** Syn. with DEWEYLITE (p. 312.)

**GYPSUM.**  $CaSO^4 \cdot H^2O$ , or  $CaO.SO^2 + 2HO$ . *Sulphate of lime. Alabaster. Selenite. Satin spar. Schaumkalk. Plaster of Paris.*—This mineral occurs both crystalline and massive. The crystals belong to the monoclinic system. Ratio of axes  $a : b : c = 1.445 : 1 : 0.5976$ . Inclination of clinodiagonal to principal axis =  $81^\circ 26'$ ;  $+P : +P$  in clinodiagonal principal section =  $138^\circ 44'$ ;  $-P : -P$  in the same =  $143^\circ 28'$ ;  $\infty P : \infty P$  in the same =  $68^\circ 46'$ . Ordinary combinations  $\infty P. [\infty P \infty] . +P. -P$  (fig. 301, p. 155) and  $\infty P. [\infty P \infty] . -P$  (fig. 302). Twins like figure 333 (p. 162). Cleavage very distinct, parallel to  $[\infty P \infty]$ . (Kopp's *Krystallographie*, p. 306.)

Hardness = 1.5. Specific gravity = 2.314–2.328. Lustre of  $[\infty P \infty]$  pearly and shining; of the other faces sub-vitreous. Massive varieties often glistening, sometimes dull, earthy. Colour usually white, sometimes grey, flesh-red, honey-yellow, ochre-yellow, blue; impure varieties often black, brown, red or reddish-brown. Streak white. Transparent in various degrees down to perfect opacity. The transparent varieties are called *Selenite*; the fine massive varieties, *Alabaster*; the fibrous, *Satin spar*. *Schaumkalk* is a variety in small scales having a pearly lustre.

Gypsum contains 46.51 per cent.  $SO^2$ , 32.56  $CaO$ , and 20.93 water; or 54.56  $SO^4$ , 24.51  $Ca$ , and 20.93 water. In the gypsum of the volcano of Albay, island of Luzon, De la Trobe found 6.43 per cent. silica.

Before the blowpipe gypsum becomes white, exfoliates, and falls to powder. At a very high temperature it melts with difficulty to a white enamel. The white powder obtained by heat hardens to a compact solid when moistened. Gypsum dissolves in 400–500 pts. water.

Gypsum often forms extensive beds in secondary countries, and is also found in tertiary and recent deposits, occasionally in crystalline rocks. It is also a product of volcanoes, occurring about fumaroles or where sulphur-gases are escaping, being formed from the sulphuric acid generated therefrom, and the lime afforded by the decomposing

lavas, lime being contained in augite and labradorite. Gypsum is also produced by the decomposition of pyrites when lime is present, and often about sulphur-springs where sulphydric acid is emitted, this gas changing, through reaction with vegetable matter, into sulphuric acid. Gypsum is also deposited on the evaporation of sea-water and brines.

Fine specimens of selenite are found in the salt-mines of Bex in Switzerland, at Hall in the Tyrol, in the sulphur mines of Sicily, in the gypsum-formation near Oçana in Spain, in the clay of Shotover Hill near Oxford; large lenticular crystals are found at Montmartre near Paris. Alabaster occurs at Castellino, 35 miles from Leghorn. Fibrous gypsum occurs in Cheshire and Derbyshire, in the red-sandstone near Moffat, in the Forth river, near Belfast, &c. Scaly foliated gypsum (*Schaumkalk*) occurs with selenite at Montmartre. Gypsum occurs in extensive beds in several states of North America, particularly in New York, Ohio, Illinois, Tennessee, and Arkansas, and is usually associated with salt-springs. Gypsum occurs altered to calcespar.

Plaster of Paris, or gypsum, heated and ground up, is used for making moulds, taking casts of statues, medals, &c., and for producing a hard finish on walls; also in the manufacture of artificial marble, as the scagliola tables of Leghorn, and in the glazing of porcelain. Alabaster is used for making statues and vases. Fibrous gypsum, when cut *en cabochon* and polished, forms an artificial gem resembling cat's-eye. (Dana, ii. 379.)

**GYROLITE or GUROLITE.** A mineral closely related to apophyllite. It occurs in spherical concretions having a lamellar radiate structure, white and pearly. Hardness = 3 to 4. Before the blowpipe and with acids it behaves like apophyllite. Analysis gave 50.70 per cent.  $\text{SiO}_2$ , 1.48  $\text{Al}_2\text{O}_3$ , 33.24  $\text{CaO}$ , 0.18  $\text{MgO}$  and 14.18 water, agreeing approximately with the formula  $3(2\text{CaO} \cdot 0.3\text{SiO}_2) \cdot 8\text{H}_2\text{O}$ , or  $3(\text{Ca}'\text{SiO}_4 \cdot 2\text{SiO}_2) \cdot 8\text{H}_2\text{O}$ . (Anderson, Phil. Mag. [4] i. 101.)

**GYROPHORIC ACID.** (Stenhouse, Phil. Trans. 1849, p. 393; Jahresb. d. Chem. 1849, p. 458.)—An acid obtained from two lichens, *Gyrophora pustulata* and *Lecanora tartarea*, which are collected abundantly in Norway for the manufacture of archil. To prepare the acid, the lichen is macerated with milk of lime; the strained liquid is treated with hydrochloric acid; and the resulting red-brown gelatinous precipitate, after washing and drying, is heated nearly to boiling with weak alcohol, to remove a green resin, then with animal charcoal and strong alcohol, which leaves undissolved a brown humus-like substance. The filtered solution deposits gyrophoric acid in crystals, which may be purified by repeated crystallisation from alcohol, with help of animal charcoal.

Gyrophoric acid forms small, soft, colourless crystals having neither taste nor smell. It is nearly insoluble in water, even at the boiling heat, very slightly soluble in ether and in cold alcohol, more soluble in boiling alcohol. It is a very weak acid; its solutions do not redden litmus, and the addition of the smallest quantity of potash or ammonia gives them an alkaline reaction. It is nearly insoluble in ammonia, dissolves in excess of potash or baryta-water, and is precipitated unaltered by acids.

By boiling with excess of potash or baryta-water, it is resolved into carbonic acid and orein; but when boiled with a very small quantity of an alkali, it is converted into an acid of intermediate composition, soluble in water, having a distinct acid reaction, and differing from gyrophoric acid in crystalline form. Gyrophoric acid is reddened by chloride of lime. When exposed to the air in contact with excess of ammonia, it is slowly converted into a purple substance. Boiled for some time with strong alcohol, it yields (besides orein and a resin) a product having the characters and composition of orsellate of ethyl,  $\text{C}^{10}\text{H}^{12}\text{O}^4$  (q. v).—With wood-spirit, it yields the corresponding methyl-ether.

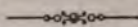
Stenhouse assigns to gyrophoric acid the formula  $\text{C}^{30}\text{H}^{18}\text{O}^{15}$ . Gerhardt (*Traité*, iii. 818) regarded it as identical, either with lecanoric acid,  $\text{C}^{15}\text{H}^{10}\text{O}^7$ , or with evernic acid,  $\text{C}^{17}\text{H}^{10}\text{O}^7$ , to the latter of which it certainly approximates closely (analyses 60.81, 61.16, and 61.12 per cent. carbon, 4.90, 5.20 and 5.0 hydrogen; calculation for  $\text{C}^{17}\text{H}^{10}\text{O}^7$ , 61.44 C, 4.82 H, and 33.74 O).

**GYROTROPE.** A name applied to various contrivances for reversing the direction of an electric current, converting a continuous into an interrupted current, separating the two currents of an induction-coil, &c.

**GYTGE.** A peculiar mud, mixed with organic matter, found at the end of the Sandefjord in Norway. After drying at  $100^\circ\text{C}$ . it contains 16.29 per cent. matter soluble in water and hydrochloric acid, 9.92 water and organic matter, and 73.80 sand and decomposed clay. (A. and H. Strecker, Ann. Ch. Pharm. xcv. 177.)



## ADDENDA.

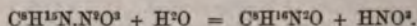


**CONINE.** The following new observations on this alkaloid have been made by Th. Wertheim (Ann. Ch. Pharm. cxxiii.; Rép. Chim. pure, 1863, p. 45):

The conine was prepared from fresh hemlock seeds (p. 2), and rectified several times in a current of hydrogen. It was perfectly limpid and colourless, or very slightly coloured. It remained unaltered for months, and could even be distilled in an oil-bath in contact with the air. It boiled at  $163.5^{\circ}$  C. under a barometric pressure of 739 mm. Conine does not dissolve a trace of chloride of calcium, which may therefore be used to dry it.

**Azoconhydrine.**  $C^8H^{16}N^2O^4$ .—Nitrous anhydride passed into pure conine is absorbed in large quantity, and after the excess has been expelled by a current of carbonic anhydride at  $30^{\circ}$  or  $40^{\circ}$  C., a molecule of conine,  $C^8H^{16}N$ , is found to have absorbed exactly one molecule of nitrous anhydride. Water extracts nitric acid from the product; and if the remainder be washed several times with water, then with dilute carbonate of sodium, dilute hydrochloric acid, and again with water, it leaves a yellow oil, rather lighter than water, having an aromatic odour and burning taste, and without action on vegetable colours.

This substance is azoconhydrine. Its composition is most simply expressed by the formula  $C^8H^{16}N^2O$ , which is that of conine + H + N + O. The nitrous anhydride probably unites in the first instance directly with the conine, forming the compound  $C^8H^{16}N.N^2O^2$ , which is subsequently decomposed by the water, yielding nitric acid and azoconhydrine:

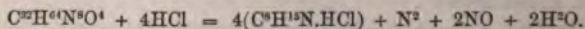


Ordinary commercial conine treated as above does not yield azoconhydrine, a violent decomposition taking place after a certain amount of nitrous gas has been absorbed. This effect perhaps arises from the presence of methyl-conine (p. 6).

The formula of azoconhydrine,  $C^8H^{16}N^2O$ , may be derived from that of conhydrine,  $C^8H^{17}NO$ , by the substitution of 1 at. N for 1 at. H; but its vapour-density, 22.25 (obs.), show that this formula must be quadrupled, making it  $C^{32}H^{64}N^4O^4$ , which for a condensation to 2 volumes, gives as the calculated density, the number 21.62.

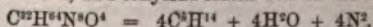
Azoconhydrine is as poisonous as conine, but appears to act more slowly. It is insoluble in water, soluble in alcohol and ether, and dissolves without alteration in strong hydrochloric and sulphuric acids, whence it is precipitated unchanged by water. Ammonia and the fixed alkalis neither dissolve nor decompose it, even with the aid of heat. When heated above  $200^{\circ}$  C. it decomposes, giving off strongly alkaline vapours, which have the odour of conine.

Dry hydrochloric acid gas converts azoconhydrine into hydrochlorate of conine, eliminating at the same time a gas which contains 1 vol. nitrogen to 2 vols. nitric oxide:



The same gas passed into a solution of azoconhydrine in anhydrous ether, forms a magma of white shining crystals, apparently consisting of hydrochlorate of ethyl-conine, resulting from the intervention of the ether.

**Conylene.**  $C^8H^{14}$ .—This compound is produced by the action of phosphoric anhydride on azoconhydrine. When the latter substance is heated to  $80^{\circ}$  or  $90^{\circ}$  C., with excess of phosphoric anhydride, pounded glass being added to moderate the action, nitrogen gas is rapidly evolved, and conylene distils over in the form of a yellowish oil:



Conylene is a yellowish oil, having a pungent disagreeable odour, of specific gravity

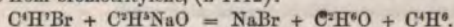


0.7007 at 18° C., insoluble in water, soluble in alcohol and ether, boiling at 120° under a pressure of 738 mm. Vapour-density, obs. = 3.80; calc. (2 vols.) = 3.56.

Bromine unites energetically with conylene, forming a product containing more than 2 at. bromine. Dibromide of conylene,  $C^8H^{14}Br^2$ , is obtained by gradually adding alcoholic bromine to a well-cooled alcoholic solution of conylene till the mixture retains a faint yellow colour after agitation, precipitating with water, washing with dilute potash and then with water, dissolving in ether, drying the mixture with chloride of calcium, and expelling the ether by evaporation in vacuo. It is a liquid of specific gravity 1.5679 at 16.25° C., having a disagreeable odour, somewhat like that of mustard, insoluble in water, soluble in alcohol and ether. Treated with pulverised hydrate of potassium it yields a liquid which, after two rectifications in a current of hydrogen, is perfectly colourless, lighter than water, and has very nearly the composition of oxide of conylene,  $C^8H^{14}O$ .

Conhydrine,  $C^8H^{14}NO$ , is perhaps a compound of oxide of conylene with ammonia; and conine,  $\left\{ \begin{smallmatrix} C^8H^{14} \\ H \end{smallmatrix} \right\} N$ , might perhaps be produced by the action of ammonia on bromide of conylene.

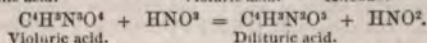
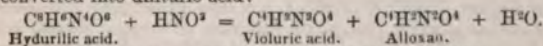
**CROTONYLENE.**  $C^8H^6$ . (E. Caventou, Ann. Ch. Pharm. cxxvii. 347.)—A hydrocarbon, homologous with allylene,  $C^3H^4$ , related to crotonic acid,  $C^4H^4O^2$ , in the same manner as ethylidene,  $C^2H^4$ , to acetic acid, and to tetrylene,  $C^4H^6$ , in the same manner as acetylene to ethylene. It is produced by the action of ethylate of sodium on bromotetrylene, the reaction being precisely analogous to that by which Sawitsch obtained allylene from bromotrietylene, (i. 1112):



Crotonylene is liquid below 15° C., but volatilises very quickly if not surrounded by ice. It has a very strong, slightly alliaceous odour, boils at about 18° C., and distils between 18° and 24°. Vapour-density, obs. = 1.936; calc. (2 vols.) = 1.868.

It unites very energetically with bromine. When bromine is dropped into crotonylene cooled by a freezing mixture, dibromide of crotonylene,  $C^8H^6Br^2$ , is obtained, as a liquid heavier than water, distilling between 148° and 158° C. with evolution of hydrobromic acid, and leaving a residue of charcoal.—This liquid left for some days in contact with excess of bromine is converted into the tetrabromide,  $C^8H^6Br^4$ , a crystalline compound isomeric with dibromide of dibromotetrylene,  $C^4H^2Br^2Br^2$ , which it also much resembles; but the latter distils undecomposed between 148° and 158° C., at which temperature, as already observed, the bromide of crotonylene is partly decomposed; moreover dibromide of dibromotetrylene does not volatilise at ordinary temperatures, even when kept for months in an open dish; and the same is the case with the isomeric compound obtained by passing the vapours resulting from the decomposition of amylac alcohol-vapour at a red heat, into bromine; but dibromide of crotonylene volatilises completely under these circumstances in 10 or 12 days.

**DILITURIC ACID.**  $C^4H^2N^2O^3$ .—This acid, discovered by Schlieper (p. 330), has lately been more fully investigated by Baeyer (Ann. Ch. Pharm. cxxvii. 211), who obtains it by the action of nitric acid on hydrilic acid. Hydrilic acid dissolves in nitric acid of ordinary strength, with copious evolution of nitrous vapours, forming a yellow solution. As soon as the evolution of gas has ceased, and a sample of the liquid forms with ammonia, no longer a reddish but a white precipitate, the liquid is left to itself, and on cooling, solidifies to a mass of crystalline laminae, which when pressed and recrystallised from a small quantity of hot water, yield pure diluturic acid. The mother-liquor retains alloxan, together with a small quantity of diluturic acid, which may be obtained by precipitation with ammonia or ferrous sulphate. The reaction takes place in two stages, violuric acid being formed in the first instance, and afterwards converted into diluturic acid:

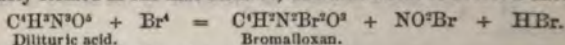


Schlieper obtained diluturic acid by boiling alloxantin with hydrochloric acid and treating the resulting crystals with nitric acid (p. 331). It was probably formed in this case by the action of the nitric acid on hydrilate of ammonium resulting from the action of the hydrochloric acid on dialuric acid (p. 316), contained in the alloxantin. (See HYDRILIC ACID.)

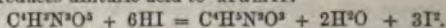
Diluturic acid crystallises in colourless quadratic prisms and laminae, containing 6 at. water ( $C^4H^2N^2O^3.6H^2O$ ). The crystals effloresce when exposed to the air, and dissolve easily in hot, more slowly in cold water, forming a deep yellow solution. It is less soluble in alcohol, insoluble in ether. When heated it decomposes, with evolution of nitrous vapours, and leaves a brown red mass.

Diluturic acid is easily recognised by the deep yellow colour with which it discolours water, and more especially in dilute potash: also by forming a white precipitate of ammonium-salts, a white precipitate composed of needle-shaped crystals with *f* sulphate, and a lemon-yellow precipitate with *acetate of silver*.

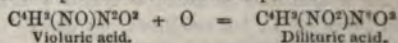
Diluturic acid exhibits the characters of a nitro-compound: when heated *hypochlorite of calcium*, it yields considerable quantities of chloropicrin (i.e. some of its salts explode violently when heated; and its amount of nitrogen can be determined by ignition with soda-lime.—When *bromine* is added to diluturic acid suspended in cold water, a very loosely combined compound is formed, which is separated from the aqueous solution by ether, and is so unstable, that a few drops of benzene separate the whole of the diluturic acid from the ethereal solution. In its original state, bromobenzene being probably formed at the same time. But diluturic acid is heated to 100° C. with bromine and a small quantity of water in a sealed tube, it is resolved into nitric acid and bromalloxan, the compound N being probably formed in the first instance, and afterwards converted into nitric



*Hydriodic acid* reduces diluturic acid to uramil:



This reaction and the preceding are analogous to those exhibited under similar circumstances by violuric acid (*q. v.*). In fact, these two acids differ only by one oxygen, and the formation of diluturic acid from violuric acid (p. 965) is simply the conversion of a nitroso-compound into a nitro-compound:



Diluturic and violuric acids mixed in hot concentrated solution unite and form a compound,  $\text{C}^4\text{H}^2\text{N}^2\text{O}^9$ , a very unstable compound, which is partly resolved into component acids when recrystallised from water.

*Diluturates*.—Diluturic acid is tribasic, but it is especially inclined to form salts containing only one atom of metal. Of these acid salts the sodium-salt is the most soluble, the others being sparingly soluble or insoluble. The diluturates have a yellow or yellow colour, and are remarkably stable, the acid not being separated from the mineral acids.

*Diluturate of Ammonium*,  $\text{C}^4\text{H}^2(\text{NH}^4)\text{N}^2\text{O}^3$ , is formed as a white crystalline precipitate on mixing diluturic acid with ammonia or an ammonium-salt; from dilute solutions it separates in concentrically grouped prisms. It is very slightly soluble in cold, somewhat more in hot water, and crystallises therefrom in small crystals and shining laminae. It is not altered by ammonia or by nitric acid; in sulphuric acid it dissolves without decomposition, and is precipitated therefrom by water. Dilute potash dissolves it, with evolution of ammonia, forming a deep yellow liquid containing dipotassic dialurate; strong potash-solution colours it yellow without dissolving it. When heated it burns away with deflagration.

*Diluturate of Barium* separates on mixing diluturic acid with acetate of barium in slender needles, which are decomposed by soluble sulphates, but not by free sulphuric acid. Chloride of barium converts this salt into a double salt,  $\text{C}^4\text{H}^2\text{BaN}^2\text{O}^3 \cdot \text{BaCl}_2$ , which may also be obtained in beautiful heavy crystals resembling twin-crystals of gypsum, on mixing a hot solution of diluturic acid with chloride of barium. The crystals give off their water at 140° C.

*Diluturate of Calcium*,  $\text{C}^4\text{H}^2\text{CaN}^2\text{O}^3$ , obtained by precipitating acetate of calcium with diluturic acid, forms slender white needles containing 4 at. water, half of which is given off at 140° C.

*Diluturate of Copper*,  $\text{C}^4\text{H}^2\text{CuN}^2\text{O}^3 \cdot 6\text{H}^2\text{O}$ , is obtained by mixing diluturic acid with a soluble copper-salt, as a white precipitate composed of slender needles with green iridescence. It gives off its water at 100° C. and explodes at a higher temperature.

*Diluturates of Iron*. The *ferric* salt,  $\text{C}^4\text{H}^2(\text{Fe}^3)\text{N}^2\text{O}^3$ , or  $\text{C}^4\text{H}^2/\text{FeN}^2\text{O}^3$ , is precipitated on adding diluturic acid to a solution of ferric chloride, in small, light yellow needles, nearly insoluble in cold, sparingly soluble in hot water. Between 110° and 120° it gives off its water and assumes a brick-red colour, and at a stronger heat it explodes.

The *ferrous* salt,  $\text{C}^4\text{H}^2\text{FeN}^2\text{O}^3 \cdot 8\text{H}^2\text{O}$ , is formed on mixing diluturic acid with ferrous sulphate, as a white precipitate consisting of slender needles, and having a greenish streak of green. It is very sparingly soluble in water, and is not decomposed by dilute sulphuric acid. At 120° C. it gives off 6 at. water, becoming dark brown, and at higher temperature it deflagrates. It also gradually loses its water when left over sulphuric acid, but quickly recovers it on exposure to moist air.

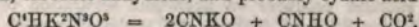
*Diluturate of Lead* is a yellowish white precipitate.

*Diluturates of Potassium*.—The *monopotassic* salt,  $\text{C}^4\text{H}^2\text{KN}^2\text{O}^3$ , is obtained



white crystalline precipitate on adding hydrochloric acid to a solution of dilituric acid in potash. It is also formed on mixing dilituric acid with the solution of any potassium-salt, separating especially from dilute solutions in large cubes, which however do not appear to belong to the regular system. It is nearly insoluble in cold water, sparingly soluble in hot water, and contains no water of crystallisation.

The *dipotassic salt*,  $C^4HK^2N^3O^3$ , which was examined by Schlieper, separates in spherical groups of beautiful yellow needles on adding alcohol to the hot lemon-yellow solution of dilituric acid or of the ammonium-salt in potash-ley. It is insoluble in alcohol and in strong potash-ley; water decomposes it partially, abstracting potash and converting it into the monopotassic-salt. When heated to a certain temperature, it decomposes, as observed by Schlieper, with slight detonation, and is resolved into cyanate of potassium, carbonic anhydride, and probably cyanic acid:



It likewise explodes when moistened with strong sulphuric acid. The solution of this salt precipitates ferrous and cupric sulphates, but the precipitates consist, not of dimetallic salts, but of mixtures of the acid potassium-salt with an acid diliturate of iron or copper.

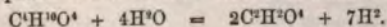
*Diliturates of Silver.*—The *monoargentic salt*,  $C^4H^2AgN^3O^3 \cdot 2H^2O$ , is obtained by adding dilituric acid to nitrate of silver, and separates from somewhat dilute solutions in well-developed prisms.—When dilituric acid is added to a warm solution of acetate of silver, a yellow precipitate of triargentic salt is first formed: but this dissolves in excess of dilituric acid, and as the solution cools, the acid salt crystallises in colourless needles. It is sparingly soluble in cold, moderately soluble in hot water. When heated it turns yellow and decomposes with explosion.

The *triargentic salt*,  $C^4Ag^2N^3O^3$ , is produced on mixing dilituric acid with excess of a hot solution of acetate of silver, as a lemon-yellow precipitate composed of needles, anhydrous and sparingly soluble in water. It explodes somewhat violently when heated, but not by percussion.

*Diliturate of Sodium*,  $C^4H^2NaN^3O^3$ , is most easily prepared by mixing the hot concentrated solutions of dilituric acid and acetate of sodium, and crystallises on cooling in long, colourless, silky needles, forming an interlaced mass when dry. It may also be obtained by decomposing the barium-salt with sulphate of sodium. It dissolves easily in water, and effloresces when left over oil of vitriol. It appears to contain 4 at. water of crystallisation.

**ERYTHROMANNITE** (p. 504).—The following method of preparing this substance is given by V. de Luynes (Compt. rend. lvi. 803). Erythric acid (p. 502) washed and drained is mixed with a quantity of milk of lime somewhat less than sufficient to decompose it completely, and heated for about two hours to  $150^\circ C$ . in a closed iron vessel; the exclusion of the air during the reaction prevents the formation of a large quantity of resinous matter. The liquid, filtered to separate carbonate of calcium, and evaporated at a gentle heat, deposits orcin in fine crystals; and the mother-liquors yield by further evaporation a crystalline mass of orcin and erythromannite, from which the former may be dissolved out by ether.

Erythromannite exhibits in a high degree the phenomenon of *surfusion*, that is to say, it remains liquid when cooled a considerable number of degrees below its melting point. Heated with potash to  $240^\circ C$ . it is resolved into oxalic acid and hydrogen:



The aqueous solution of erythromannite in contact with platinum-black, absorbs oxygen so rapidly that the mass becomes incandescent; with a dilute solution, the action is less violent and yields an acid.

The iodide of tetryl formed by the action of hydriodic acid on erythromannite (p. 595) acts strongly on acetate of silver, yielding tetrylene and acetate of tetryl. The latter when decomposed by potash yields tetrylic alcohol, identical with that obtained from tetrylene, not with that produced by fermentation (De Luynes). (See TETRILIC ALCOHOL.)

**ETHYL, IODIDE OF** (p. 533).—Messrs. Rieth and Beilstein (Ann. Ch. Pharm. cxxvi. 250) prepare this compound by introducing into a flask 10 pts. of amorphous phosphorus, 50 pts. alcohol of 90 per cent., and 100 pts. iodine, leaving the mixture to itself for 24 hours, and then distilling. The distillate thus obtained is but slightly contaminated with free iodine, and yields very nearly the theoretical quantity of iodide of ethyl.

**ETHYL, PROTOSULPHIDE OF** (p. 545).—This compound, heated with fuming nitric acid, dissolves, with evolution of red vapours, but without forming a trace of sulphuric acid; and the solution evaporated nearly to a syrup, solidifies on cooling



to a crystalline mass, consisting of diethylsulphone  $C^2H^4SO^2$  (analogous to phobenzide  $C^{12}H^{16}SO^2$ ). This compound crystallises easily from water or alcohol, thin, colourless, tabular crystals several inches long; melts at  $70^\circ C.$ ; boils at  $248^\circ$ ; great resistance to the action of oxidising substances. It may be distilled unchanged from fuming nitric acid. Nascent hydrogen reduces it to protosulphide of ethyl.

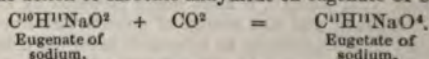
With nitric acid of specific gravity 1.2 a different action takes place, the sulphide dissolving easily at ordinary temperatures, without much evolution of gas, and without its penetrating odour. The product formed appears to be analogous in composition to nitrate of tellurethyl. The solution gently heated with *ferricyanide of potassium* free alkali, yields on cooling crystals which appear to consist of diethylsulphone.—The same solution reduces *chromate of potassium*, the liquid on cooling depositing rhombic tables, the composition of which has not yet been determined.—*Ferric chloride* added to the nitric acid solution produces an abundant separation of oily drops which solidify in the crystalline form on cooling, and probably consist of dichloride of sulphethyl  $(C^2H^4)^2SCl^2$ , analogous to dichloride of selenethyl. (A. v. Oefele, Ch. Pharm. cxxvii. 370.)

**ETHYLENE, IODOCHLORIDE OF.**  $C^2H^4Cl$ .—This compound, described p. 579, as obtained by the action of chloride of iodine on iodide of ethylene, is likewise produced by the action of chloride of iodine on ethylene-gas, namely by passing gas through an aqueous solution of chloride of iodine, washing the red oil which falls to the bottom with caustic potash, and distilling. That which passes over above  $14^\circ$  is iodochloride of ethylene.

This compound has a density of 2.151. Heated with alcoholic potash, it yields iodide of potassium, and gives off a gas burning with a green-edged flame, probably chloroethylene.  $C^2H^3Cl$ .

Tritylene obtained from glycerin yields in like manner iodochloride of tritylene (Maxwell Simpson, Proc. Roy. Soc. xii. 278; Rép. Chim. pure, 1863, p. 500.)

**EUGETIC ACID.**  $C^{10}H^{12}O^4$ . (Scheuch, Ann. Ch. Pharm. cxxiv. 14.)—This acid obtained by the action of carbonic anhydride on eugenate of sodium:



Sodium is dissolved in eugenie acid contained in a retort through which a current of carbonic anhydride is passing, the action being assisted towards the end by a gentle heat. The cooled mass dissolved in warm water and heated with hydrochloric acid yields an oil which is a mixture of eugenie and eugetic acids. It is agitated several times with solution of carbonate of ammonium, and evaporated with addition of carbonate of ammonium; hydrochloric acid is then added, the liquid shaken up with ether, the ethereal solution evaporated, and the crystalline residue recrystallised from boiling water. The product is not very abundant.

Eugetic acid crystallises from its hot aqueous solution in long colourless prisms, melts at  $124^\circ C.$ , is sparingly soluble in cold water, very soluble in alcohol and ether. Its solutions have an acid reaction. The aqueous solution is coloured blue by ferric chloride. The acid is resolved by heat into eugenie acid and carbonic anhydride.

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